

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

SEPTEMBER 1925.

LI. *On the Effect of Chemical Constitution on the X-Ray Spectrum of Sulphur.* By B. RAY, D.Sc., Lecturer in Physics, Calcutta University*.

[Plate XVII.]

§1. *Introduction and Experimental Results.*

AS is well known, the phenomena of X-ray spectra are almost but not quite independent of the physical and chemical state of the element under investigation. This effect appears primarily in the wave-lengths of the absorption edges, and has been subject to a number of investigations in Professor Siegbahn's laboratory. As would be expected from theoretical considerations, the effect on the wave-lengths of the emission lines is much smaller. Still, a perceptible influence was detected in a recent investigation by the writer†, who, using the precision X-ray spectrograph of Siegbahn, was able to detect a small difference in the wave-lengths of $K\alpha_1$ and $K\alpha_2$ in a number of elements when investigated under different conditions. This difference was especially conspicuous in the distance between the two lines known as the relativity doublet, whereas the absolute shift of the lines was not determined with great accuracy. On account of the theoretical interest of the problem of the origin of this doublet, the writer has extended the investigation to the case of sulphur where, partly due to the

* Communicated by Prof. N. Bohr.

† Phil. Mag. Jan. 1925.

variability of its chemical compounds and partly due to its small atomic number, large effects might be anticipated, and where the absolute as well as the relative shift could be determined more easily.

The apparatus used was a vacuum spectrograph with metal X-ray tube of Professor Siegbahn's construction. The high vacuum in the X-ray tube was separated from the low vacuum in the spectrograph by goldbeaters' skin. Since the sulphur rays are very easily absorbed in air, an auxiliary oil-pump was used to have the vacuum in the spectrograph as high as possible. The salt under investigation was pressed on the anti-cathode in the form of powder in the usual way. As is, however, well known, salts placed on the anti-cathode disappear rapidly and are apt to undergo chemical alterations, and a special type of anti-cathode was therefore used containing four faces, each of which was covered with salts at the beginning of the experiments, and one after the other could be exposed to the cathode rays by simply turning the anti-cathode from the outside in its vacuum-fitting. Another new addition to the spectrograph consisted in a metallic shutter placed just before the photographic plate but supported independently by the base of the spectrograph. This shutter, constructed by Mr. Olsen of this laboratory, allowed two exposures to be obtained on one and the same plate, one just above the other, without the risk of any shift in position of the plate. This was of special importance for the direct comparison of the spectra of the different sulphur compounds.

Calcite was used as a crystal, and in order to ensure sharp images the crystal was during the exposure slowly turned to and fro through an angle of about one degree.

In order to measure the wave-lengths of sulphur lines, the cobalt lines were taken as reference. In fact, the $K\alpha_1$ and $K\alpha_2$ lines of sulphur in the first order appear on the plate between the $K\alpha_1$ and $K\alpha_2$ lines of Co in the third order. The wave-lengths of the sulphur lines would therefore be obtained by interpolation from Siegbahn's precision measurements of the Co lines. As a check of this method, the said wave-lengths were also calculated by means of the distance from the photographic plate to the crystal, which for this purpose could be easily found with sufficient accuracy.

The results of the measurements are given in Table I. The accuracy in the measurements is generally of the order 0.06 X-unit. The second decimal has therefore been printed in small figures.

TABLE I.—Wave-length in X-units.

Compound.	α_2 .	α_1 .
S	5363·8 ₅	5360·9 ₁
	5363·8 ₈	5360·9 ₀
	5363·8 ₇	5360·9 ₀
	5363·9 ₀	5360·9 ₁
	5363·9 ₁	5360·9 ₁
Mean ...	5363·90	5360·90
CaS	5363·9 ₀	5360·90
FeS	5363·8 ₇	"
CuS	5363·9 ₀	"
SrS	5363·9 ₂	"
MoS	5363·8 ₆	"
Ag ₂ S	5363·9 ₁	"
SnS	5363·9 ₀	"
Sb ₂ S ₃	5363·9 ₀	"
Sb ₂ S ₅	5363·9 ₁	"
BaS	5363·8 ₇	"
PbS	5363·9 ₀	"
Mean ...	5363·90	
Na ₂ SO ₄	5360·90	5358·5 ₁
K ₂ SO ₄	"	5358·4 ₈
CaSO ₄	"	5358·4 ₆
Fe ₂ (SO ₄) ₃	"	5358·5 ₃
CuSO ₄	"	5358·4 ₆
SrSO ₄	"	5358·5 ₀
Ag ₂ SO ₄	"	5358·5 ₄
BaSO ₄	"	5358·4 ₆
PbSO ₄	"	5358·4 ₈
Mean ...		5358·50
Na ₂ SO ₃	5360·90	5358·5 ₀
CaSO ₃	"	5358·4 ₆
CuSO ₃	"	5358·4 ₆
Ag ₂ SO ₃	"	5358·4 ₈
CdSO ₃	"	5358·4 ₈
BaSO ₃	"	5358·5 ₀
PbSO ₃	"	5358·5 ₃
Mean ...		5358·50

As will be seen, the values for the various types of compounds agree very closely with each other. As regards pure sulphur, no difference could be observed between rhombic and plastic sulphur. As seen from the table, also no difference could be ascertained between pure sulphur and sulphides of various metals. Similarly the values for the

various sulphates and sulphites agree closely with each other. However, a very marked difference appeared between sulphur and sulphides on the one hand and sulphates and sulphites on the other. This difference consisted not only in a shift of the position of the doublet, but also in a change of its width. Thus, as a mean result of our measurements, we have found for sulphur or sulphides $\Delta\lambda = 3.0 \text{ X.U.}$, and for sulphites or sulphates $\Delta\lambda = 2.4 \text{ X.U.}$ The shift of the position of the whole doublet was so large that on the plates the $K\alpha_1$ line of sulphur coincided with considerable accuracy with the $K\alpha_2$ line of a sulphate. As a consequence of this, the plate will exhibit three lines instead of four when a mixture of sulphide and sulphate is present on the anti-cathode. Owing to the reduction of the salts under the bombardment of the cathode-rays, photographs of long exposures of sulphates or sulphites show besides two stronger lines also a third faint line at the position of $K\alpha_2$ for a sulphide. (See Pl. XVII. *a, b, c, d.*)

This observation raises the question as to the extent to which chemical changes on the anti-cathode may influence the results. Thus it might be imagined that the identity of the spectra obtained with sulphite or sulphate, or with sulphur or sulphide, is due to the one form being in a very short time converted into the other. However, no trace of additional faint lines could be observed, even if the material on the anti-cathode was frequently renewed.

Another interesting feature is exhibited by the lines $K\alpha_3$ and $K\alpha_4$. Their wave-lengths are always found to be the same whether they are excited in sulphur crystals or sulphides on the one hand or sulphites or sulphates on the other. The only difference lies in the fact that in the former case the lines are sharp, while in the latter case they are somewhat diffuse, the edge of the lines on the side of short wave-lengths being somewhat less sharp than the edge on the side of long wave-lengths. Although this want of sharpness is probably due to alterations in the chemical state, the experiments leave hardly any possibility for doubting that in the much smaller influence of the chemical state on the lines $K\alpha_3$, $K\alpha_4$ compared with the lines $K\alpha_1$, $K\alpha_2$ we are dealing with an essential difference in the behaviour of these lines, to the reason for which we shall come back in the following.

§ 2. Discussion of the Results.

Making use of Lindh's* measurements of the position of the K-absorption edge in sulphur and sulphates, the results

* Dissertation, Lund, 1923.

of our measurements allow us to calculate the following values for the L_{II} and L_{III} levels expressed in the Rydberg frequency as unit for CuS and $CuSO_4$.

	Sulphide.	Sulphate.	Difference.
K (Lindh)...	181.85	182.68	0.83
L_{II}	11.96	12.70	0.74
L_{III}	11.87	12.62	0.75

In the first place it will be seen that the change in the levels is quite considerable, being for the K-levels about $\frac{1}{2}$ per cent. and for the L-levels about 9 per cent. The theoretical interpretation of this change has to be sought in the changes of the binding of the electrons in the M-group. It is of interest, however, to point out that the changes are still small compared with the change to be expected if the behaviour of the sulphur atom in a sulphate compound could be simply compared with that of a six-fold charged sulphur atom.

In fact a simple estimate of the effect of the "outer screening"* to which the presence of the M-electrons in the neutral sulphur atom gives rise leads to a weakening influence on the binding of the K- and L-electrons which amounts to about one-half of the value of the L-levels themselves and thus is almost ten times larger than the difference in the levels observed in sulphur and sulphate. Even if for many purposes it is convenient to regard the sulphur atom in the sulphate molecule as a six-fold charged ion, it is thus clear that the presence of the electrons which in this picture are assigned to the oxygen atoms will exert a compensating influence on the energy necessary to remove an inner electron from the sulphur atom which is nearly as large as that exerted by the M-electrons in the neutral sulphur atom.

Compared with the shift of the levels, the shift of the emission lines themselves is very small, as is also to be expected from the theory, since the outer screening effect will be practically the same for a K-electron and an L-electron. As seen from the table, the experiments bring out that the K-level is changed slightly more than the L-levels. Considering, however, what we have just termed the compensation of the outer screening effect on the levels, it is hardly possible at present to offer any simple explanation of the small difference under consideration.

* Comp. Bohr, and Coster, *Zs. für Phys.* 1923.

Due to the narrowness of the L-doublet, its change does not appear clearly from the table, but, as mentioned in the former section, the doublet is quite considerably affected by the chemical state, its width being 3.0 X.U. in sulphur and only 2.4 X.U. in sulphates. As regards the interpretation of this result, it must be emphasized that we do not at present possess any simple interpretation of the remarkable fact that the L-doublets are given with such close approximation by Sommerfeld's formula for the relativity influence of the binding of an electron moving round a point-charge. Compared with this formula, we may express our result by saying that the magnitude of this point-charge is almost a half unit larger for sulphur than for sulphates, or, in other words, that the so-called relativity screening constant is about 0.6 unit larger for sulphate than for sulphur. It is interesting to note that this change is of the same order of magnitude as the difference of the total inner screening responsible for the so-called screening doublet L_I L_{II} in the L-series. Not only the difficulties which at present stand in the way for a simple interpretation of the screening and the relativity doublets*, but also the difficulty of theoretically estimating the influence of the compensating effect referred to above seems to make any attempt of a closer interpretation illusory. At present it can only be a question of collecting material which perhaps will be of value for a future theory of the origin of the doublets. In this respect the observations in the present paper may give information of the same character as the observations of Siegbahn and Ray† as regards the anomalous behaviour of the K relativity doublet for the elements of the iron family, and also of the $L\alpha$ -doublet‡ for the palladium family and the rare earths. Although the latter result undoubtedly offers an interesting general confirmation of Bohr's explanation of the singular position of these families within the periodic table, no quantitative interpretation can at present be given.

Before concluding we may still draw attention to the difference in the behaviour of the lines $K\alpha_3$, $K\alpha_4$ compared to that of $K\alpha_1$, $K\alpha_2$ mentioned in the former section. This difference may be brought to an interesting connexion with the interpretation of the former lines advocated by Wentzel, according to which these lines originate from atoms in

* Compare Bohr and Coster (*l. c.*).

† *Ark. f. Mat. Astr. och Fys.* Bd. xviii. no. 14.

‡ *Phil. Mag.* Oct. 1924.

which both K-electrons are removed. In fact, the increase in the charge of the sulphur atom accompanying this removal may be expected to have a large influence on the orbits of the looser-bound electrons in the neutral sulphur atom and in the sulphate molecule. In this respect the small shift in the lines under consideration might suggest that the ionization would produce an essential change in the constitution of the sulphate molecule to the effect of making the sulphur atoms behave similarly as in the isolated state. This may be connected with the fact that a sulphur atom which has lost both K-electrons may be able to bind 8 M-electrons with a considerable strength similar to that of the binding of the M-shell in the neutral argon atom. Due, however, to circumstances of the same kind as those playing a part in the effect discussed above, it would seem difficult to reach a simple theoretical interpretation.

§ 3. *Summary.*

The wave-lengths of the K-lines of a great number of sulphur compounds have been examined. It is found that the wave-lengths of the rays within the limits of experimental error are the same for sulphur and sulphide compounds on one hand and for sulphites and sulphates on the other, but that considerable differences are exhibited by the two classes of compounds, the lines $K\alpha_1$ and $K\alpha_2$ being shifted to shorter wave-lengths for the latter class at the same time as their distance apart is considerably diminished. For the lines $K\alpha_3$ and $K\alpha_4$ no such shift was observed. A general discussion as regards the theoretical interpretation of the results is given.

It gives me great pleasure to thank Professor N. Bohr for his many valuable suggestions during the whole course of the work. My thanks are also due to Mr. Y. Nishina for his unfailing friendly help and interest during the work, and to Professor G. Hevesy for kindly supplying me with the sulphur compounds for this investigation.

Universitetets Institut for teoretisk Fysik,
Copenhagen,
June 1925.

LII. *Note on Production of Atomic Nitrogen and its Arc Spectrum.* By K. T. COMPTON, *Professor of Physics, Princeton University**.

TWO years ago the writer, in collaboration with Dr. P. S. Olmstead†, succeeded in obtaining an atmosphere of atomic hydrogen at low pressure within a tungsten tube heated to about 2200° C., and measured the critical radiating potentials of atomic hydrogen by the method of electric impacts within this tube. This success led us to attempt a similar experiment in nitrogen. The possibility of thermally dissociating molecular nitrogen depends upon its heat of dissociation, which was then unknown, but was believed to be high. Langmuir‡, for instance, states that practically every hydrogen molecule which strikes a hot tungsten filament is dissociated, whereas he could detect no evidence of such dissociation in the case of nitrogen at any temperature attainable with a tungsten filament, although he could have detected as much as 5 per cent. of dissociation. Nevertheless there was a chance that, within a high-temperature enclosure, a detectable degree of dissociation might be attained.

The results of two years of work on this problem have been entirely negative. We have succeeded, by the former method, in obtaining beautiful radiating potential curves of nitrogen (and also of carbon monoxide in several cases where the water-cooling of the apparatus was insufficient to keep cool a Khotinsky wax joint), but there was no evidence of any effect which could be ascribed to nitrogen in the atomic state.

Very recently Eucken§ has shown that the heat of dissociation of N_2 into N is about 440 kg. cal. per mol. as compared with 90 in the case of hydrogen. This value is so high as to show the utter futility of further attempts along the lines mentioned above.

Another very different method of obtaining atomic nitrogen is suggested by the dissociation of hydrogen which is effected by collisions of the second kind with excited atoms of mercury, as described by Cario and Franck||, Duffendack and Compton¶, and Turner**. This case illustrates a generalization which Franck†† added to the original theory of "collisions

* Communicated by the Author.

† Phys. Rev. xxii. p. 559 (1923).

‡ Journ. Am. Chem. Soc. xxxvi. p. 1708 (1914), xxxvii. p. 417 (1915).

§ *Ann. der Chemie*, 440, p. 111 (1924).

|| *Zs. f. Phys.* xi. p. 161 (1922).

¶ Phys. Rev. xxiii. p. 583 (1924).

** Phys. Rev. xxiii. p. 464 (1924).

†† *Zs. f. Phys.* ix. p. 259 (1922).

of the second kind" developed by Klein and Rosseland*. According to this theory, if any excited atom collides with a different atom or molecule, its energy of excitation may be transformed into kinetic, chemical, or excitation energy of the impacted molecule. The probability of thus effecting a chemical or excitation change seems to be the greatest if the energy of the original excited atom is just sufficient to effect the given change, and diminishes as the available energy more and more exceeds the necessary amount. The calculations of Turner indicate that practically every collision of an excited mercury atom with a hydrogen molecule results in its dissociation.

Now Eucken's value for the heat of dissociation of nitrogen corresponds to 19.05 in equivalent volts. There is no atom which is known to exist plentifully in an excited state of greater energy than this, under attainable laboratory conditions, except helium. This gas has been shown by numerous experiments to possess minimum excitation states of 19.73 and 20.56 volts energy, both existing in relatively large concentration in electrical discharges through helium at pressures of the order of 1 millimetre or more. Thus, if nitrogen were mixed with helium under conditions favourable for excitation of the helium, we should expect the nitrogen to be effectively dissociated by energy transferred from the excited helium atoms at collisions of the second kind.

Conditions favourable for this process may readily be predicted. To secure a large effect, a large electronic current through the gas is necessary. (It is well known that electrons are much more efficient agents for excitation and ionization than are positive ions.) In order to obtain large electron currents, ionization is necessary for neutralization of space charge around the cathode. If the gas-pressure is low, the necessary amount of ionization may occur by impact of electrons against normal helium atoms, since a sufficient number of electrons can, in the long free path, acquire energy exceeding the minimum ionizing energy corresponding to 24.5 volts. At higher gas-pressures, the chance of thus acquiring the ionizing energy is less, since a larger proportion of the electrons lose their energy by exciting helium atoms to the 19.7 and 20.5 volt states. In this condition, more of the ionization is of the cumulative or two-stage type, which becomes predominant at pressures above a few millimetres†. It can be shown‡, for instance, that an

* *Zs. f. Phys.* iv. p. 46 (1921).

† K. T. Compton, *Phys. Rev.* xx. p. 284 (1922); *Phil. Mag.* xliii. p. 531 (1922).

‡ K. T. Compton, *Phys. Rev.* xxii. p. 333 (1923).

electron moving in a field of 50 volts /cm. through helium at 1 mm. pressure would make, on an average, three collisions after attaining the minimum exciting energy but before acquiring the minimum ionizing energy. If the gas-pressure were increased to 20 mm. the corresponding number of collisions would be 1200. These figures, combined with the fact that excitation is very probable and ionization very improbable at impacts by electrons whose energy only slightly exceeds the critical amount, illustrate the great importance of excited states and cumulative ionization at the higher helium pressures. Thus large current and high helium pressure are favourable to dissociation by action of excited helium atoms on nitrogen.

On the other hand, it is obvious that *low* partial pressure of nitrogen is necessary. If the nitrogen were present in too large proportion, the electrons would collide inelastically with nitrogen molecules, and thus lose their energy without effecting the excitation of the helium. This is, of course, the explanation of the fact that the spectrum of a helium discharge-tube containing a trace of foreign gas shows the lines of the foreign gas with greatly increased intensity. The helium atoms serve simply to increase, by elastic collisions, the total path of electrons through the tube, and thus increase the chance of collision with a molecule of foreign gas. It is only when the proportion of gas is extremely small that the electrons attain the energies required for excitation of the helium itself. Calculations similar to those above show that, as the helium pressure is increased, the amount of nitrogen must be diminished if most of the electrons are not to lose their energy directly to the nitrogen. At 20 mm. helium pressure, rough calculations show that the nitrogen pressure should be less than 0.01 mm., probably considerably less, in order to have most of the electron energy go directly into the helium. On the other hand, the amount of nitrogen must be sufficient to be appreciable.

These considerations suggest that there should be a rather limited range of conditions which are favourable, in a discharge-tube, to the production of atomic nitrogen in appreciable quantity by collisions of the second kind. If Eucken's value for the heat of dissociation is correct, helium should be the only gas capable of producing this association. Although the actual amount of nitrogen thus dissociated would of necessity be small, the *percentage* dissociation should be very high, since the chance of meeting of two nitrogen atoms would be much less than the chance of meeting with an excited helium atom, under the conditions postulated.

In this state of dissociation we should expect to find the

spectrum of neutral atomic nitrogen strongly developed, owing to the favourable conditions for impact of electrons against the neutral atoms.

Since the appearance of Eucken's paper, the writer has been considering the possibilities outlined above, and was preparing to put them to an experimental test, when he read the very recent paper by Merton and Pilley* on "Experiments relating to the Spectrum of Nitrogen." These authors have, in a very elegant research, discovered that a new and distinct line spectrum of nitrogen is obtained only if the following conditions are fulfilled:—

(1) The nitrogen must be present in very small amount, mixed with helium at a pressure of about 30 mm.

(2) A condensed discharge (therefore large current density) must be used.

(3) The gases must be extremely pure, the slightest trace of impurities such as organic matter serving to bring out spectra of the impurities. (Only a trace of neon was present as an impurity.)

(4) If the nitrogen is too plentiful, the new line spectrum is replaced by the molecular band spectrum.

(5) If argon is substituted in place of helium, the new line spectrum is not obtained.

It is striking that every one of these conditions is exactly in line with the above considerations based on collisions of the second kind, and they were, in fact, predicted before the paper by Merton and Pilley appeared. The experimental work of these authors may therefore be considered as still another evidence of the importance of collisions of the second kind in the field of ionization and excitation.

The explanation of their experiment suggested by Merton and Pilley is, in effect, that the helium limits the electron velocities to about 20 volts, which may be the most favourable speed for exciting the nitrogen arc spectrum. Besides being less complete than the explanation suggested in the present paper, there is definite experimental evidence against it. In experiments both with two-electrode arcs and three-electrode tubes, in both of which the electron currents and speeds could be independently regulated over wide ranges, Duffendack† and Duffendack and Duncan‡ have failed to find any evidence of line excitation at these voltages, and have not found any except spark lines to be excited at higher voltages. It is true that they probably had no appreciable proportion of atomic nitrogen present in their experiments. However, if the presence of sufficient atomic nitrogen could

* Proc. Roy. Soc. A, cvii. p. 411 (1925).

† Phys. Rev. xx. p. 665 (1922). ‡ Phys. Rev. xxiii. p. 295 (1924).

be accounted for as the direct result of electron impacts, it is probable that they and others would have succeeded in exciting the new arc spectrum, as, for instance, the line spectrum of hydrogen may be excited.

The peculiarity of nitrogen appears to be, as pointed out by Merton and Pilley, that it dissociates under electron impacts into ions rather than atoms*. This, together with the well-proved fact that excitation is a much more prominent process than recombination in producing spectra†, accounts for the fact that ordinary excitation of nitrogen gives only the molecular band and the atomic spark spectra.

These considerations may be considered as supporting Eucken's value of the heat of dissociation of nitrogen. Had its value been as low as 280 kg. cal. per mol., we should have expected argon to be as effective as helium in the above experiment.

Finally, two extensions of this work suggest themselves. If neon should behave as does helium in bringing out the nitrogen arc spectrum, we may conclude that the heat of dissociation is as low as 370 kg. cal. per mol.; if it does not the value lies between this and 450, in agreement with Eucken. Thus spectroscopic observations may give some evidence regarding heats of dissociation. Furthermore, Eucken's value of 425 for the heat of dissociation of oxygen suggests that an arc spectrum of atomic oxygen might be obtained by similar experiments with this gas in helium. In this case, however, it is possible that the electron affinity of atomic oxygen may prevent its existence in the neutral atomic state in any considerable quantity. Likewise CO, with heat of dissociation 415, may give interesting spectra of C and O when properly mixed with helium. It seems possible that many spectroscopic peculiarities of mixtures of molecular with monatomic gases, such as the "comet-tail" spectrum, may find explanation of the sort suggested above.

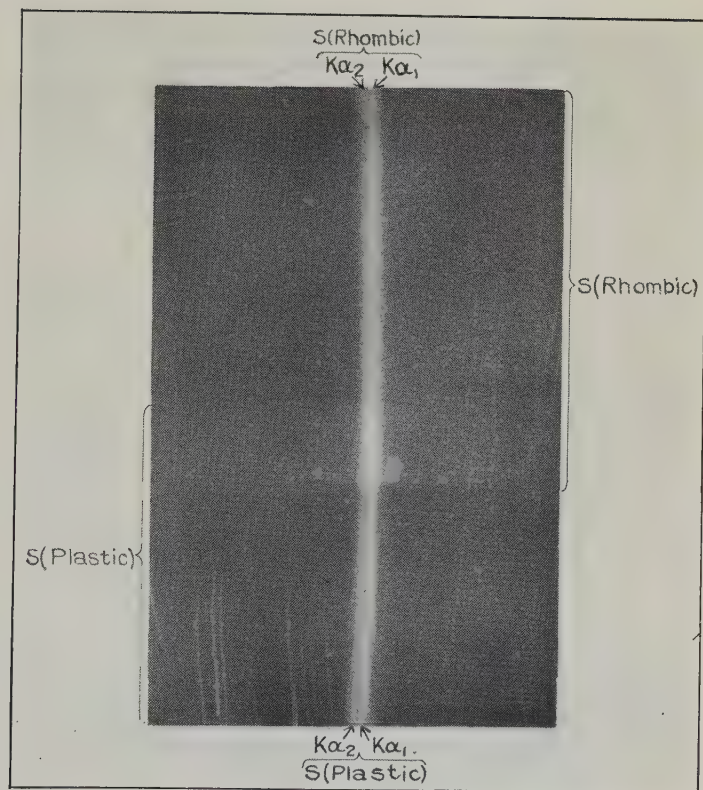
Palmer Physical Laboratory,
Princeton, N.J., U.S.A.

Note.—After this paper was written, the author found that Prof. M. N. Saha and Mr. N. K. Sur had previously suggested the desirability of investigating the action of excited helium on nitrogen, with especial reference to the possible production of the N line spectrum. It may be said, however, that the probable significance of the relation between the heat of dissociation of N_2 and the energy of excited helium was then unknown for lack of knowledge regarding the heat of dissociation. (See *Phil. Mag.* xlviii. p. 427, 1924.)

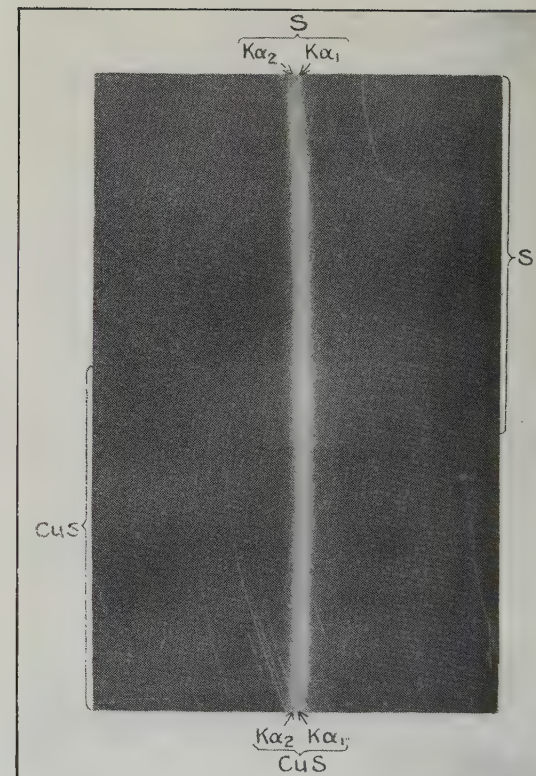
* Smyth, *Proc. Roy. Soc. A*, civ. p. 121 (1923).

† Compton, Turner, and McCurdy, *Phys. Rev.* xxiv. p. 597 (1924).

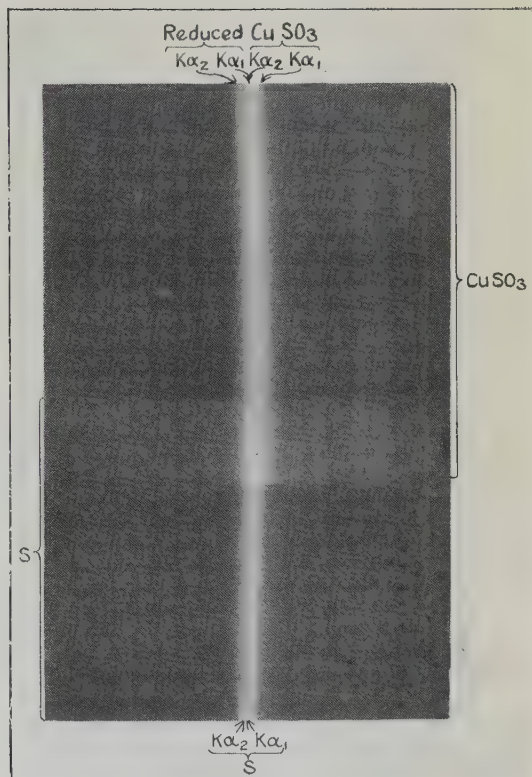
(a)



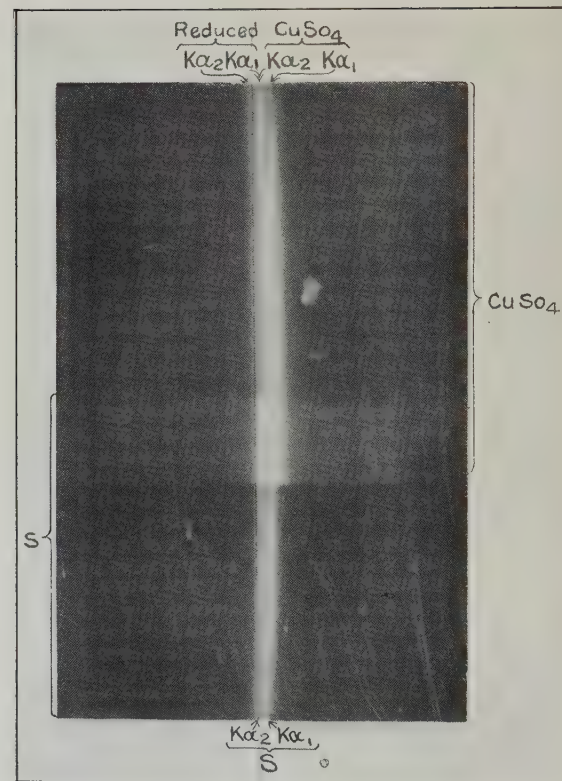
(b)



(c)



(d)



LIII. *The Orientation of Crystals in Metal Test-Pieces subjected to Small Strains followed by Heat-Treatment.* By C. F. ELAM, M.A., *Armourers and Brasiers Research Fellow* *.

IN the following paper a comparison has been made of the orientations of crystals of aluminium, an aluminium-zinc alloy containing 18 per cent. zinc, and iron which have been formed by the method of straining followed by heat-treatment, with the object of ascertaining whether the method of manufacture influenced the orientation. It is known from the work of Polanyi† and others that, with severe cold work such as occurs in wire-drawing, the crystals tend to assume certain definite positions relative to the direction of stress, and Glöcker‡ has shown recently that on annealing such material this orientation is not completely obliterated. Edwards and Pfeil§, in describing their tests on iron crystals, were of the opinion that there was a similarity in the orientation, and concluded that the small crystals in the aggregate which eventually grew were so related to the axis of pull that they underwent a type of deformation which favoured crystal growth. The question as to whether the large crystals were formed from new crystal nuclei, *i.e.* by a process of recrystallization or from some of the original small crystals, was discussed by Professor Carpenter|| and the author in a previous paper. A similarity of orientation would favour the latter view rather than the former.

Altogether the axes of sixty-four crystals have been determined and compared. The majority of the pure aluminium crystals determined were those occupying the whole parallel portion of a test-piece, but in one case all the crystals in a test-piece containing four were determined. In the case of iron, the axes of six crystals in one strip, kindly sent to the writer by Professor C. A. Edwards, were determined by Mr. R. L. Aston in the Cavendish Laboratory, Cambridge, who has kindly allowed his results to be included, in addition to other crystal axes determined by the writer. Of the alloy crystals, all were turned out of bars consisting of several crystals.

The method of determining the crystal axes in a test-piece has already been described¶. It is unnecessary to give the actual figures, as these in themselves do not show clearly how

* Communicated by the Author.

† Ettisch, Polanyi, and Weissenberg, *Zeit. für Physik*. iv. & vii. 1921, etc.

‡ Glöcker, *Zeit. für Physik*, xxxi. (1925).

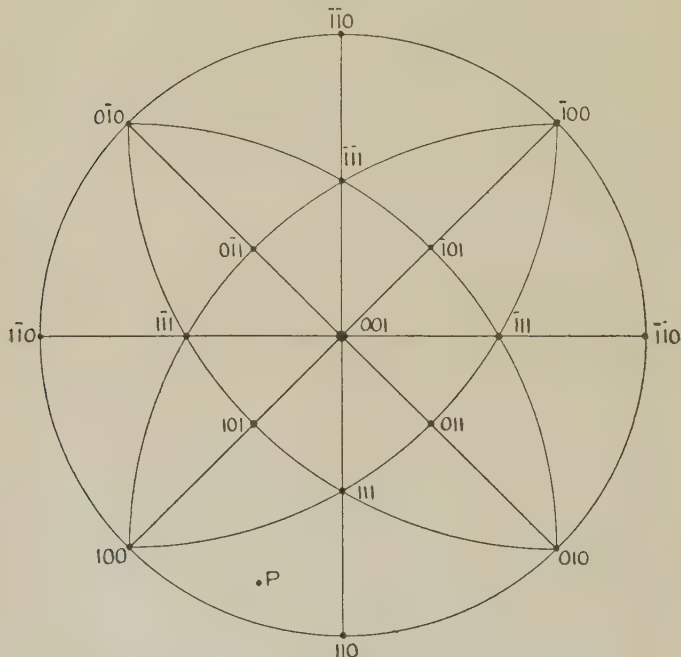
§ Edwards and Pfeil, *Journ. Iron & Steel Inst.* 1924, no. 1.

|| Carpenter and Elam, *Proc. Roy. Soc. A*, c. (1921).

¶ Müller, *Proc. Roy. Soc. A*, cv. (1924).

the crystals vary in relation to the axis of the test-piece. For this purpose the stereographic projection of the crystal axes was made in which one of the cubic (100) axes was in the centre of the figure, and the four octahedral (111) axes were arranged symmetrically round it* (fig. 1). In order to fit the crystal axes determined by X-rays on to this figure, it is necessary to rotate them (using a stereographic net) until one of the cubic (100) axes coincides with the centre of the diagram. The axis of the test-piece is then represented by a point P lying in one of the twenty-four spherical triangles in the figure. These triangles are all similar, and by choosing

Fig. 1.



a suitable cubic axis to put in the centre of the figure, the axes of all the test-pieces can be made to fall into one particular triangle, when their relative positions can be more easily compared. Figs. 2, 3, 4, and 5 each represent one of these triangles, in which the positions of the axes of the test-pieces have been marked. It will be at once apparent that a great variety of orientation is met with, although in the case of aluminium most of the crystals favour a position near the (110) axis, and none have yet been obtained near a (100) axis. Several of the alloy and

* Taylor and Elam, *Proc. Roy. Soc. A*, cviii. (1925).

Fig. 2.—Pure aluminium.

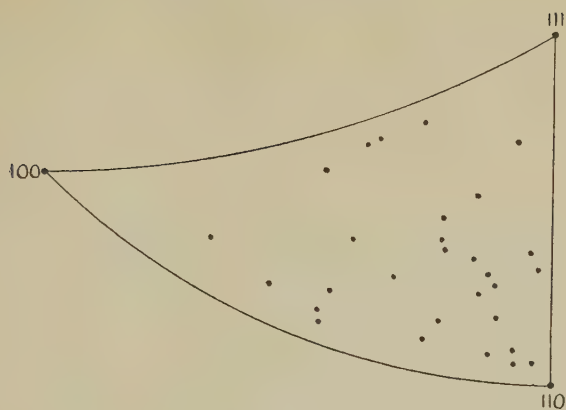
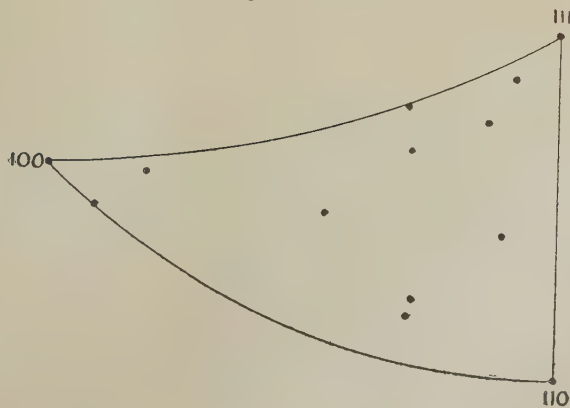


Fig. 3.—Aluminium test-piece consisting of four crystals.



Fig. 4.—Iron.



iron crystals, however, were near this position. It is possible that the rate of growth is more rapid in some directions than others, so that the majority of the largest

Fig. 5.—Aluminium-zinc alloy.



crystals produced may favour one orientation. This question could only be decided after an examination of a large number of crystals of varying sizes. As has been pointed out, all test-pieces in fig. 2 were single-crystal test-pieces, but those in the other diagrams represent considerable variations in size, and there appears to be no relation between crystals in the same test-piece. Furthermore, some experiments described by Professor Carpenter and the writer* showed that the orientation of a crystal could be changed by straining and heat-treating, and that the new orientation appeared to have no relation to that of the original crystal. The process is the same as that of converting an aggregate of small crystals into one crystal. It is not, however, possible to say how this re-orientation takes place.

Summary.

The results of the determination of the crystal axes of sixty-four crystals produced by a process of straining followed by heat-treatment show that the variety of orientation is great, although it is possible that some directions are more favoured than others. The direction of straining does not influence the orientation of the crystals to the extent that was expected.

Royal School of Mines,
June 15th, 1925.

* Carpenter and Elam, *Proc. Roy. Soc. A*, cvii. (1925).

LIV. *The Heating Effect of the γ -Rays of Radium B and Radium C.* By C. D. ELLIS, Ph.D., Fellow and Lecturer in Trinity College, Cambridge, and W. A. WOOSTER, B.A., Hugo de Balsham Student and J. M. Dodds Student of Peterhouse, Cambridge *.

INTRODUCTION.

IN this paper we describe measurements of the heating effects of the γ -rays of radium B and radium C. The main difficulty was to find a method of measuring the γ -ray heating separately and not superimposed on the very much greater α -particle heating effect of radium C. This was accomplished in the present experiments by means of an automatic compensation of the α -particle heating.

It is the object of this introduction to point out that this measurement has an importance beyond that of determining the fraction of the disintegration energy emitted as γ -rays, since, combined with other measurements, it leads to a knowledge of the absolute intensities of the different γ -rays.

It is generally accepted that the quantum dynamics apply to the nucleus and that the emission of γ -rays consists in the emission of discrete quanta $h\nu_1, h\nu_2, \dots$ so that the relative intensities of the different γ -rays must mean the relative number of quanta emitted. But this discrete emission accompanies the disintegration of the nucleus, itself a discrete phenomenon, making it possible in this case to speak of the absolute intensities in the sense of the probabilities p_1, p_2, \dots that any one disintegration will be accompanied by the emission of one quantum of frequency ν_1, ν_2, \dots . It is unnecessary to stress the importance of knowing these probabilities, they describe the entire phenomenon of emission and would lead to an immediate interpretation of the sets of nuclear stationary states which are responsible for the emission of the γ -rays.

These probabilities can only be found by a combination of three different measurements, namely, the heating effect of the γ -rays, the relative intensities of the β -ray lines, and the coefficient of internal conversion of the γ -rays in the parent atom. To see this we must consider the γ -ray emission in more detail. When an atom disintegrates with emission of a quantum of frequency ν , then in the majority of cases this quantum escapes from the atom, but there is a certain probability α that it will be converted inside the

* Communicated by Prof. Sir E. Rutherford, F.R.S.

parent atom and give rise to a fast electron. This probability of internal conversion was discussed by Ellis and Skinner* (Proc. Roy. Soc. A, cv. p. 186, 1924), who showed that in a typical case of radium B it must be greater than one-tenth, and Gray ('Nature,' Jan. 3rd, 1925) found even greater values for radium D. The natural β -ray spectra are due to this internal conversion, and we may express the relative intensities (*i. e.*, number of electrons) of the different β -ray lines in the general form

$$\frac{I_1}{I_2} = \frac{p_1 \alpha_1}{p_2 \alpha_2}; \quad \frac{I_1}{I_3} = \frac{p_1 \alpha_1}{p_3 \alpha_3}, \text{ etc.}$$

This statement must be extended to cover the fact that the γ -ray may be converted in any of the electronic levels, so we define the appropriate coefficients $1\alpha_K, 1\alpha_{L_I}, 1\alpha_{L_{II}}, \dots, 1\alpha_{M_V} \dots$ etc., and the intensities of the corresponding β -ray lines are in the ratio of these quantities when multiplied by the p 's. These relative intensities can be found directly from the β -ray spectra, and form one stage in the determination of the p 's. The next stage is to find the α 's, the probabilities of internal conversion. There are different methods of doing this which will not be entered into here; instead we turn to the last measurement by which these relative intensities can be turned into absolute ones. For this purpose it is necessary to find the total energy E emitted per sec. in the form of γ -rays by a known quantity of radioactive material. Suppose the quantity is such that n atoms are disintegrating per sec., then

$$E = n\{h\nu_1 \cdot p_1[(1 - 1\alpha_K)(1 - 1\alpha_{L_I})(1 - 1\alpha_{L_{II}})\dots] + h\nu_2 \cdot p_2[\dots]\}.$$

This quantity E is of course the heating effect of the γ -rays, measurements of which are described in this paper, and it is at once seen how essential a position it occupies in the problem of the absolute intensities.

There is an alternative measurement which can take the place of the heating effect, and that is to determine the total number, Q , of γ -rays emitted. This could be represented as

$$Q = n\{p_1[(1 - 1\alpha_K)(1 - 1\alpha_{L_I})\dots] + p_2[\dots]\}.$$

Kovarik* has recently carried out this experiment, and reference will be made later to his results which are in substantial agreement with ours. Experiments to determine the relative intensities of the γ -rays are in progress.

GENERAL CONSIDERATIONS.

During the course of their work on the heating effect of the α -rays of radium C, Rutherford and Robinson* found it necessary to make experiments to determine the order of magnitude of the heating effect of the γ -rays, which are also emitted by radium C. Their method was to measure first the effect due to the α -rays, the γ -rays being allowed to escape, and then to absorb a certain fraction of the γ -rays by means of lead screens and find the increase in the total effect. These experiments were difficult to carry out, but still it was possible to show that the γ -ray heating effect must be about 7 per cent. of the total and that under practical conditions of incomplete absorption of the γ -rays a maximum increase of only 4 per cent. was to be expected when the lead screens were added. These figures bring out clearly the impossibility of obtaining any accuracy by a subtraction method; in fact, to obtain a final 5 per cent. accuracy in the γ -ray heating it would be necessary to carry out both the main measurements with an accuracy of about 1 in 500. It is very difficult to obtain such an accuracy in this type of experiment, and so the only other alternative was adopted, that of finding a method by which the γ -ray heating could be measured independently of that of the α -rays. The general principle is not difficult to find since the α -rays are easily absorbed whereas the γ -rays are penetrating, so that if an absorber, such as a block of lead, were placed some distance from the source the only heating effect in it would be due to the γ -rays. In practice, however, the matter is not so simple, as the following figures show. Suppose a small tube containing 100 millicuries of radium emanation is taken as a source. The total γ -ray energy emitted by the disintegration products radium B and C is about 0.8 calorie an hour, and even with the lead block placed only 6 mm. from the source it is not practicable to absorb more than 1/8 of the γ -rays, giving a heating effect of 0.10 calorie an hour. But the heating effect of the α -rays from the emanation, radium A, and radium C is over 10 calories an hour, and even if the α -rays are prevented from leaving the immediate neighbourhood of the source, the problem still remains of measuring a very small heating effect of 1/10 calorie an hour in the presence of a source generating heat at a rate 100 times as great. Various methods of shielding were tried but they were not successful, the heat radiated from the source always being in excess of that produced by

* Rutherford and Robinson, *Phil. Mag.* [6] xxv. p. 312 (1913).

the γ -rays. We therefore adopted a slightly different principle which finally proved quite successful. Instead of trying to remove the α -particle heating we arranged for an automatic compensation of its effect.

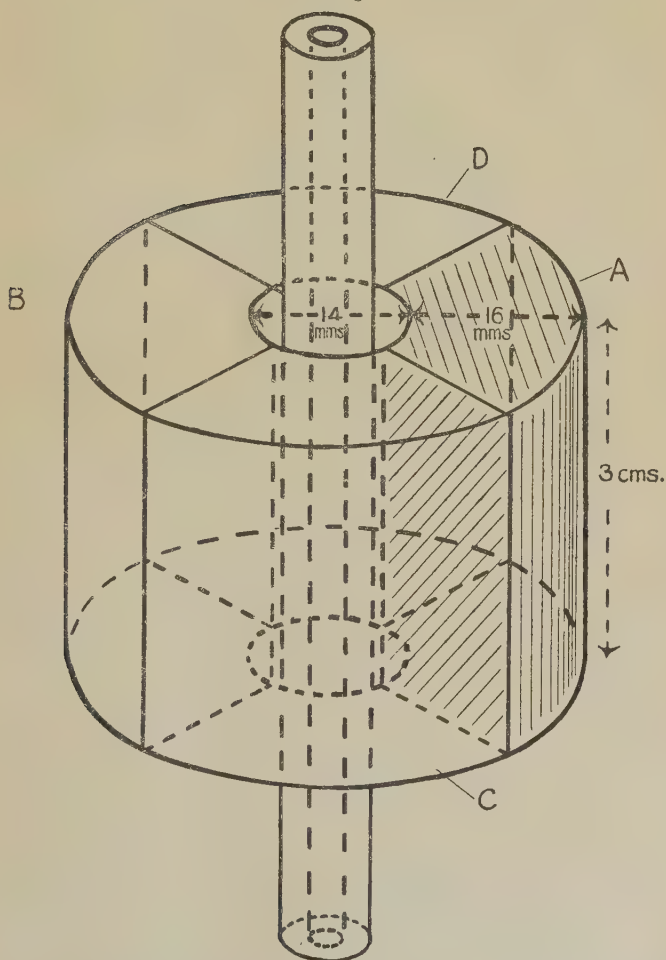
Apparatus.

The actual calorimeter consisted of a hollow circular cylinder made out of four equal sectors, and is shown diagrammatically in fig. 1. Two opposing ones A and B were respectively of lead and aluminium, and they were insulated from one another by the two other sectors C and D of Balsa wood. The aluminium sector had holes bored in it so as to make it have the same heat capacity as the lead sector. This composite cylinder was fixed inside another closely fitting cylinder of Balsa wood and caps of Balsa wood placed at each end. The whole fitted inside a thick copper case. Nineteen silver-constantan thermocouples in series were wound round the composite cylinder so as to record any temperature difference of the lead and aluminium sectors. Through the centre hole of the composite cylinder ran an 8 mm. copper rod, bored throughout its length with a 3 mm. hole. This rod was supported at its two ends by the outer copper case and did not touch any portion of the composite cylinder, there being a three millimetre clearance. The radioactive source, which was a small glass tube 8 mm. long filled with radium emanation, was placed in the centre hole of the copper rod. This arrangement provided an automatic compensation of the heat emission due to the α -particles, for although the central copper rod became heated, just as much heat was received from it by the aluminium sector as by the lead sector. Since these were of equal heat capacity their temperature rose by the same amount, and the galvanometer connected to the thermocouples showed no deflexion. This compensation will also hold for β -rays, since radium B and C appear to emit few if any electrons faster than 12,000 Hp, and Varder's* results show that even these are almost completely absorbed in the copper tube of 2.5 mm. thickness. The same would be true for any radiation which escaped from the copper tube but which was yet completely absorbed in the aluminium sector and hence also in the lead one. As soon, however, as the radiation is sufficiently penetrating to pass through the aluminium without being completely absorbed, as in the case of the γ -rays, then a temperature

* Varder, Phil. Mag. xxix. p. 725 (1915).

difference will be set up because the radiation will have been more absorbed in the lead and therefore have given up more heat to it. Hence, although the lead and aluminium sectors receive far more heat by radiation from the central

Fig. 1.

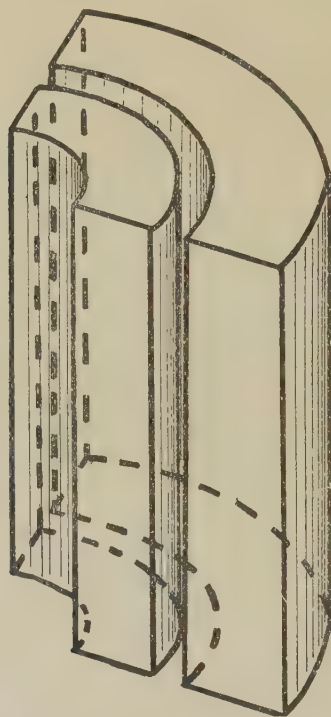


copper tube than they do by absorption of the γ -rays, the deflexion of the galvanometer, which measures the difference of temperature of the sectors, depends only on the γ -ray energy absorbed. With this arrangement the large α -particle heating can be made almost to cancel out, and

except for the necessity of rather more complicated calibration experiments with heating coils, the γ -ray heating effect could be obtained with the same ease as the total heating effect of a radioactive body.

Certain further details of the apparatus can conveniently be given at this point. Each of the metal sectors consisted of an inner and outer part as shown in fig. 2, and the

Fig. 2.



thermocouples were wound round the outer face of the inner part. In this way they registered the temperature of the centre of the metal blocks. The thermocouples were made by Wilson's method * by taking a long piece of constantan wire and silvering alternate sections, and were connected to a moving coil galvanometer of 24 ohms resistance giving 220 mm. scale deflexion at 1 metre for 10^{-6} ampere. Owing to the smallness of the main effects slight thermoelectric effects in the galvanometer became very troublesome,

* Wilson & Epps, Phys. Soc. Proc. xxxii. p. 326 (1920).

but this difficulty was overcome by placing a reversing key close to the apparatus and taking as reading the difference of the deflexions with the key in its two positions. This reversing key was especially designed to avoid thermoelectric effects inside itself.

Heating coils were sunk in the lead and aluminium sectors for calibration purposes, and the currents in them measured on calibrated direct-reading instruments. In the case of the lead two heating coils were used, one in both the inner and outer sectors, making it possible to study the effects of different distributions of heat production.

EXPERIMENTAL RESULTS.

The method of making measurements was to observe the maximum deflexion reached when the rate of heat supply was equal to the rate of heat loss. It was a disadvantage of this apparatus that it required forty-five minutes to reach this point, but the necessity for having a large mass of lead to absorb a considerable fraction of the γ -rays made it undesirable to shorten it. It was intended to employ for the final measurement a sensitive Paschen galvanometer, since the galvanometer we used for the preliminary experiments gave only 7 mm. deflexion. This small deflexion was measured by means of a travelling microscope, and the error involved was found to be less than 1 per cent. Since this error was less than the others involved in the experiment, we did not consider it necessary to use the more sensitive instrument. The actual rise curve was rather complicated, a maximum deflexion being reached in 45 minutes, after which the deflexion decreased slowly. The initial rise was approximately an exponential with a half period of 8 minutes, but if after the maximum had been reached the source of heat was taken away, there was a sharp initial fall and then a slow return with a half period of about three hours. The explanation of this behaviour lies in the fact that the galvanometer only measures the difference of temperature of the lead and aluminium, and that the temperature-time curves of the lead and aluminium sectors considered separately are somewhat complicated owing to there being heat transfer not only from the heated metals to the colder surroundings but also from the lead to the aluminium. It was not thought necessary to investigate this in more detail, it being sufficient to make the calibration measurements under exactly the same conditions as the γ -ray experiments and to verify, as we did, that the

deflexion-time curves were identical in the two cases. Readings of the deflexion were taken every two minutes over a period of an hour, and the maximum deflexion taken as the mean of the six measurements made between 40 and 50 minutes from the start.

The results for the γ -ray heating were very concordant, and are shown in Table I. The first column shows the amount of radioactive material, the second the deflexion, and the third column the values of these deflexions when increased to correspond to a source of 70.5 mg.* The origin of this particular value will become clear when we consider the calibration measurements. It can be seen that the values in column 3 agree closely, and we can take the value 6.81 mm. for the deflexion for 70.5 mg. as being correct to about 1 per cent.

TABLE I.

Value of source in millicuries.	Deflexion in mm.	Deflexion for 70.5 millicuries.
58.02	5.60	6.81
48.45	4.69	6.83
40.47	3.81	6.64
33.80	3.31	6.90
28.23	2.75	6.87
	Mean	6.81

The whole of this deflexion cannot be attributed to γ -rays, that would only be the case if the compensation of the α -particle heating were exact. This point was investigated by putting a small heating coil in place of the emanation tube and generating heat there to correspond to the α 's of about 100 mg. A deflexion of 0.8 mm. was found to result, showing that with this arrangement the disturbing effect of the α -rays was reduced to one-tenth of that of the γ -rays. This small residual effect can easily be corrected for, since the amount of the α -particle heating is known to 1 in 200. We obtained this correction at the same time as the general calibration in the following way. The small heating coil already referred to was placed in the central copper tube,

* We are greatly indebted to Mr. L. Bastings for determinations of the strength of the sources used in these experiments.

and in all the calibration experiments the same constant current sent through it so as to give a heating effect equal to that of the α 's and β 's from 70.5 mg. Various currents were then sent through the heaters in the lead block, and also the sector in the aluminium block. The result of many experiments, using either the lead or aluminium heater alone, or both combined, was that the resulting deflexion δ mm. was connected by the following equation with the heat C_{Pb} produced in the lead block, and that C_{Al} produced in the aluminium

$$\delta = 0.421C_{Pb} - 0.573C_{Al} + 0.57,$$

where C_{Pb} and C_{Al} are expressed in units of 10^{-6} cal. per sec. It may be mentioned in passing that the term 0.57 represents the residual effect of the α 's from 70.5 mg. The inequality of the coefficients of C_{Pb} and C_{Al} is due to different conditions of heat loss of the two sectors.

This calibration equation is valid for C_{Al} varying between $1/11$ and $1/3$ that of C_{Pb} , and with γ -rays the heat produced in the aluminium is about $1/7$ of that produced in the lead. It was important to investigate whether the value of the deflexion depended on the distribution of the heat production, for with the γ -rays the heat is produced throughout the body of the lead, the distribution being unequal due to absorption, whilst in the calibration experiments the heat comes from the two small heaters. It seems unlikely that any error was introduced here because the deflexion did not change when the ratio of the amount of heat produced in the inner lead heater to that in the outer varied between the limits 6 and 1.7. It was also possible that the heat conducted down the wires leading from the heaters might introduce errors, since in the γ -ray case the heaters, if anything, are at a lower temperature than the lead, whereas in the calibration experiments they are at a higher one. However, no change was produced on increasing the conductivity of the leads by a factor of 30, so any correction for this effect is unnecessary to our accuracy. Viewing the calibration experiments as a whole, we consider a reasonable estimate of the error involved to be 3 per cent.

CALCULATION OF RESULTS.

(a) *Amount of γ -rays absorbed.*

Before the deflexion obtained with a known source of γ -rays can be combined with the calibration equation to give the total γ -ray energy, it is necessary to calculate the fractions absorbed in the lead and aluminium sectors. For

this purpose we require the coefficient of true energy absorption as distinct from the scattering, *i.e.* deflexion of energy, and to be applicable to the present experiment it must have been determined over a range of 16 mm. of lead after passing through a preliminary filter of 2.5 mm. of copper. We are greatly indebted to Mr. Ahmad for measuring the total absorption coefficient under precisely these conditions. He found the value 2.64×10^{-23} for the atomic coefficient. This may be represented as the sum of three coefficients

$$(\tau + r + \sigma) = 2.64 \times 10^{-23},$$

where τ , r , and σ represent respectively the photoelectric absorption, the energy absorption in the scattering process, and true scattering. The value of the total energy absorption coefficient $(\tau + r)_{\text{Pb}}$ may be found in the following manner, as suggested by Mr. Ahmad. For aluminium his measurements give the total atomic absorption coefficient as 0.278×10^{-23} , but in this case τ is negligible, and so

$$(r + \sigma)_{\text{Al}} = 0.278 \times 10^{-23}.$$

Now the coefficients r and σ are both known to vary linearly with N , the atomic number, hence

$$(r + \sigma)_{\text{Pb}} = \frac{82}{13} (r + \sigma)_{\text{Al}} = 1.757 \times 10^{-23},$$

giving

$$\tau_{\text{Pb}} = 0.883 \times 10^{-23}.$$

It now remains to find r_{Pb} , and this may be done by deducing from the mean X-ray result

$$\tau = 2.29 \times 10^{-2} \lambda^3 N^4$$

the "effective" wave-length $\lambda = 0.0205 \text{ \AA.U.}$ Using this value, r_{Pb} can now be calculated by means of the formula

$$r = \sigma_0 N \frac{\alpha}{(1 + 2\alpha)^2},$$

$$\sigma_0 = 6.65 \times 10^{-25}, \quad \alpha = \frac{0.0242}{\lambda},$$

proposed by Compton, and strongly supported by the experiments of Owen* and of Ahmad†. The result is

$$r_{\text{Pb}} = 0.570 \times 10^{-23},$$

giving as total atomic coefficient of energy absorption for the above conditions

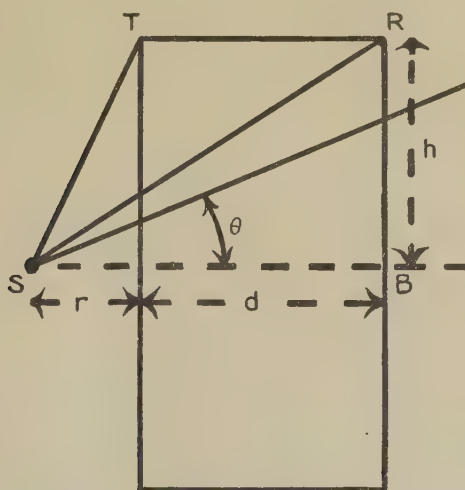
$$(0.883 + 0.570) \times 10^{-23} = 1.453 \times 10^{-23}.$$

* Owen, Phys. Soc. Proc. xxxvi. p. 355 (1924).

† Ahmad, Proc. Roy. Soc. A. cv. (1924).

The corresponding ordinary coefficient k is 0.482 cm.^{-1} , this coefficient consisting of 0.293 for the photoelectric absorption and 0.189 for energy absorption in the scattering process. The value for aluminium is less important and comes to 0.058 cm.^{-1} , when deduced from the above equations. It may be noted that this calculation does not depend on any particular picture of the scattering process, but merely on the validity of Compton's results used as interpolation formulæ. However, in view of the rather indirect method by which these values were obtained, it was thought best to carry out the further calculations with coefficients $0.482 + \delta\tau$ and $0.058 + \delta\tau'$, and to express our final result with a correcting factor involving first and second order terms in $\delta\tau$ and $\delta\tau'$. Should later work lead to slightly different values of the absorption coefficients, our experimental result can be recalculated at once by means of this factor.

Fig. 3.



The calculation was carried out first with the approximation of the source being considered as a point half-way along the axis of the cylinder, and remembering that each sector formed one quarter of the cylinder, the fraction absorbed can be written

$$\frac{1}{4} \left[\int_0^{\text{RSB}} f(\theta) \left(1 - e^{-\frac{kd}{\cos \theta}} \right) \cos \theta \cdot d\theta + \int_{\text{RSB}}^{\text{TSB}} f(\theta) \left(1 - e^{-k \left(\frac{h}{\sin \theta} - \frac{r}{\cos \theta} \right)} \right) \cos \theta \cdot d\theta \right],$$

where the symbols have the meaning shown in fig. 3.

The term $f(\theta)$ represents the initial transmission factor of the copper tube, and is included in the integrals since it is a function of θ owing to the varying thicknesses of copper traversed by the oblique rays.

The actual calculation was a little more complicated in order to take into account the gaps between the inner and outer sectors. Further, the fact was allowed for that the absorption coefficient 0.482 cm.^{-1} represents a mean value for passage through a thickness of 16 mm. at various obliquities. Assuming this value corresponded exactly to passage at 20° , small corrections were applied to give an appropriate k for every θ . After this further small corrections were applied, making in all -3 per cent., to take into account the finite length of the source, the holes bored out to contain the heaters, and the escape of electrons from the surface of the lead. It might be thought that errors would arise from the escape of the lead K radiation excited by the absorption of the γ -rays, since only the L absorption is here effective, but a short calculation shows that this correction is negligible.

The final result of the calculation can be expressed in this way. If h_γ calories per sec. be emitted by the radioactive source, then the amount absorbed in the lead and aluminium sectors is respectively $A_{\text{Pb}}h_\gamma$ and A_{Al}, h_γ , where

$$A_{\text{Pb}} = (23.44 + 32.9\delta\tau - 26(\delta\tau)^2) \frac{\pi}{4} \cdot \frac{1}{180},$$

$$A_{\text{Al}} = (2.38 + 44.1\delta\tau') \frac{\pi}{4} \cdot \frac{1}{180}.$$

(b) *Deduction of Heating Effect.*

We can now combine the three stages, the deflexion due to 70.5 mg. , *i. e.* 6.81 mm. , the calibration equation, and the fractions absorbed A_{Pb} and A_{Al} . If H_γ represents the γ -ray energy in 10^{-6} calorie per sec. emitted by 70.5 mg. , then in the calibration equation

$$\delta = 0.421 C_{\text{Pb}} - 0.573 C_{\text{Al}} + 0.57$$

we have to substitute

$$C_{\text{Pb}} = H_\gamma \cdot A_{\text{Pb}}, \quad C_{\text{Al}} = H_\gamma \cdot A_{\text{Al}}.$$

From H_γ we then obtain the γ -ray energy H_γ emitted by 1 gram of radium in equilibrium, in calories per hour

$$H_\gamma = \frac{8.62}{1 + 1.63\delta\tau - 1.3(\delta\tau)^2 - 3.0\delta\tau'}.$$

Dropping the correcting terms for possible subsequent changes in the value of the absorption coefficients, we have :

The amount of radium B and radium C that is in equilibrium with 1 gram of radium emits 8.6 calories per hour in the form of γ -rays.

We estimate this result to be correct to 5 per cent.*, and we have therefore made no correction for the transient equilibrium of the products in the emanation tube.

Division of the Energy between Radium B and Radium C.

It is important to find how this total heating effect is to be divided between radium B and radium C. A simple method of doing this is based on a knowledge of the apparent absorption coefficients of the total radium B rays, of the total radium C rays, and of the combined rays. †

Suppose E_B , E_C are the γ -ray energies emitted by the amounts of radium and radium C in equilibrium with a certain quantity of radium, and E_{BC} represents the total γ -ray energy emitted by the two bodies. If μ_B and μ_C are the respective energy absorption coefficients‡ of the corresponding γ -rays for any thickness d , then

$$\begin{aligned} E_B + E_C &= E_{BC}, \\ E_B e^{-\mu_B d} + E_C e^{-\mu_C d} &= E_{BC} e^{-\mu_{BC} d}. \end{aligned}$$

If we write

$$p = E_B/E_C,$$

then

$$p = \frac{e^{-\mu_C d} - e^{-\mu_{BC} d}}{e^{-\mu_{BC} d} - e^{-\mu_B d}}.$$

There are no measurements of these absorption coefficients available which have been made under precisely the required conditions, but a preliminary estimate may be made as follows. The one quantity we know is $\mu_{BC} = 0.482$, and the conditions to which it refers are preliminary filtering through 2.5 mm. copper and then absorption determined over 16 mm. of lead. If we use this value, then p must be taken to mean the ratio E_B/E_C after passing the filter. The value assigned to μ_B is of little importance, since $e^{-\mu_B d}$ is very small over this large thickness, but a value $\mu_B = 2.42$ may be used, calculated by the usual formulæ from the mean wave-length

* A preliminary account of this work was published in Camb. Phil. Soc. xxii. 1925, in which the value 8.1 cal./hour was given. The difference represents the result of the more detailed calculation of the absorption given here.

of the radium B γ -rays. The really important quantity is μ_c . There is no essential difficulty in measuring it under these conditions, but since it has not yet been done we must take Ahmad's* values for the absorption coefficient of the total radium B and C radiation after filtering through 1 cm. of lead. His value was 0.426, and since the 1 cm. filter will have removed all but about 2 per cent. of the radium B rays, we may take this value as μ_c . These three values $\mu_{BC} = 0.482$, $\mu_c = 0.426$, $\mu_B = 2.42$, referring to $d = 1.6$ cm., give $p = 0.10$.

If we were to consider the value $\mu_c = 0.426$ too high and take instead $\mu_c = 0.42$, we should obtain $p = 0.11$. Moseley and Robinson †, by comparing the number of ions formed in air by the softer and harder radiations of radium B and C, deduced a ratio $p = 0.074$, while a similar measurement by Miss J. Szmidt ‡ gave $p = 0.072$. There seems, then, little doubt about the general order of magnitude, but we believe the value $p = 0.10$ to be nearer the truth, since the method of calculation employed by the above authors would have tended, even more than the one used here, to attribute part of the harder radium B radiation to radium C. This conclusion receives further support from the work of Moseley and Makower §, who found that 12 per cent. of the ionization given by radium B and C, after passing through 3 mm. of lead, was to be attributed to radium B. It must be remembered that this value of p refers to the ratio after passing 2.5 mm. of copper, and so needs a correction since the radium B rays are more absorbed in the copper than those of radium C. This correction proves to be only +3 per cent., and in view of the other uncertainties may be neglected. More work is required on this important point, but accepting the above provisional value we obtain the following heating effects for radium B and radium C separately. These are also expressed in terms of volts per atom disintegrating, the values being obtained on the basis of Geiger's || recent value for the number of α -particles emitted by 1 gram of radium, i.e. 3.4×10^{10} .

Heating Effects of Radium B and Radium C.

	cals./hour.	volts/atom.
Radium B	0.86	1.85×10^5
Radium C	7.7	16.6×10^5

* *Loc. cit.*

† *Phil. Mag.* [6] xxv. p. 312 (1913).

‡ *Phil. Mag.* [6] xxviii. p. 527 (1914).

§ *Phil. Mag.* [6] xxiii. p. 302 (1912).

|| Geiger and Werner, *Zeit. für Phys.* xxi. p. 197 (1924).

DISCUSSION.

It was pointed out in the introduction that the full use of a value for the heating effect of the γ -rays could only be made in conjunction with certain other measurements, but it is useful at this stage to effect a comparison with previous determinations and to see in a general way to what extent our measurement fits in with existing views.

Our result 8.6 calories an hour is in approximate agreement with that obtained in 1914 by Rutherford and Robinson, 6.7 calories an hour; but a closer comparison is hardly justified, since the earlier measurement aimed only at settling the order of magnitude. Reference has already been made to the experiments of Kovarik, where he determined the total number of quanta of all frequencies emitted by a known quantity of radium B and C. His results are not directly comparable with ours at this stage, since the two measurements are connected by means of the relative intensities of the β -rays, and accurate measurements on this point have yet to be made. Still, it is easy to see that our measurement of the heating effect is in general agreement with his conclusion that on the average two γ -rays are emitted for every two disintegrations, one of radium B and one of radium C. For we may deduce from the work on β -ray spectra that the mean energy of the radium B γ -rays is 0.3×10^6 volts, and that of the radium C γ -rays is between 1.1 and 1.7×10^6 volts, whereas we found a total energy emission from the two bodies of 1.85×10^6 volts, which could be accounted for on the basis of one γ -ray from each body. However, we do not wish to draw any detailed conclusions until the measurements on the relative intensities of the β -rays and their internal absorption coefficients have been made.

There is one further point which may be mentioned. It has been suggested by one of us that the emission of γ -rays is due to transition between a set of stationary states in the nucleus, the latter either being left in an excited state as the result of the previous disintegration, or being put into such a state by its own disintegration. In either case this view of only one excitation, coupled with the detailed picture of the stationary states that have been given, would preclude the emission of a large number of quanta at each disintegration and would suggest rather a number close to one, in agreement with the results of Kovarik's and our experiments.

SUMMARY.

(1) The heating effect of the total γ -rays emitted by the quantity of radium B and radium C in equilibrium with 1 gram of radium has been found to be 8.6 calories an hour.

(2) Of this 0.86 calories an hour is to be attributed to radium B and 7.7 calories an hour to radium C.

(3) The importance of determining the absolute intensities of the γ -rays is pointed out, and it is shown that a knowledge of the heating effect is an essential step in the process.

We would like to thank Professor Sir Ernest Rutherford for his continual help and advice during the course of the experiments. We are indebted to Mr. G. R. Crowe for the preparation of the emanation tubes.

LV. *The Motions of Electrons in Oxygen.*

By H. L. BROSE, M.A., D.Phil., Christ Church, Oxford*.

1. **I**N the accounts of previous researches on the motion of electrons in gases which have been made in the Electrical Laboratory, Oxford, a method has been described of determining the velocity W in the direction of a uniform electric force and the velocity of agitation U of electrons in gases. The investigations of the motion of electrons in nitrogen, hydrogen, and oxygen† were among the first of these researches, and it was found that in nitrogen and hydrogen the velocities depended only on the ratio of the electric force Z to the gas-pressure p , but with oxygen the values obtained for the velocities U and W diminished as the force Z and the pressure p were increased in the same proportion. This was attributed to the formation of ions, as the ratio of the number of ions to electrons in the stream would increase with the pressure. The measurements made with the smaller gas-pressures were therefore taken as being approximately the velocities in oxygen, but the exact values of the velocities and the cause which led to the formation of the ions were not determined. It was therefore considered desirable to make further experiments with this gas, in order to find the velocities more accurately and to ascertain whether the formation of ions was due to an impurity in the gas, or is an effect which may occur in a very small proportion of collisions of electrons with molecules of oxygen.

* Communicated by Prof. J. S. Townsend, F.R.S.

† J. S. Townsend and V. A. Bailey, Phil. Mag. xlii. p. 875, Dec. 1921.

In the above experiments the electrons were obtained by the action of ultra-violet light on a metal plate, and ebonite insulation was used in the construction of the apparatus. It therefore remained to make experiments where a hot filament is used to supply the electrons, in order to eliminate any effect which the ultra-violet light may have had on the gas, and to find whether the oxygen became impure owing to some action of the gas either on the ebonite insulation or on the elastic glue which was used to make air-tight joints in the outer case of the instrument.

2. No diminution was observed in the number of ions in a stream of electrons obtained from a hot filament; and after this had been established, the effect of impurities was investigated. For this purpose two improved forms of apparatus were used where the insulation was entirely of glass, and the joints of the outer case were carefully ground to fit, so that the gas should be exposed to as little of the elastic glue as possible. These instruments had been made for the experiments on monatomic gases, and they have been fully described in the account of the experiments made on the motion of electrons in argon and hydrogen by Professor Townsend and Mr. Bailey*. The results obtained with these two instruments were in good agreement, and it was found that with carefully prepared oxygen the number of ions in the stream of electrons obtained with ultra-violet light was quite inappreciable, even when comparatively large pressures of the gas were used.

3. As examples of the measurements, the results obtained with the instrument where the stream of electrons passed through a slit at two centimetres from the receiving electrodes may be considered. Examples of the values of W and k which were obtained are given in Table I., where the determinations are arranged in groups, corresponding to the cases where the ratios of Z/p were approximately the same. The quantity k is the ratio of the energy of agitation of the electrons to the energy of agitation of a molecule of a gas at $150^{\circ}\text{C}.$, and the velocity of agitation U is obtained by the formula:

$$U = 1.15 \cdot 10^7 \sqrt{k}. \quad . \quad . \quad . \quad . \quad (1)$$

It will be noticed that k and W are independent of Z and p , provided that the ratio Z/p is constant.

* J. S. Townsend and V. A. Bailey, *Phil. Mag.* xliv. p. 1033, Nov. 1922.

TABLE I.—Oxygen.

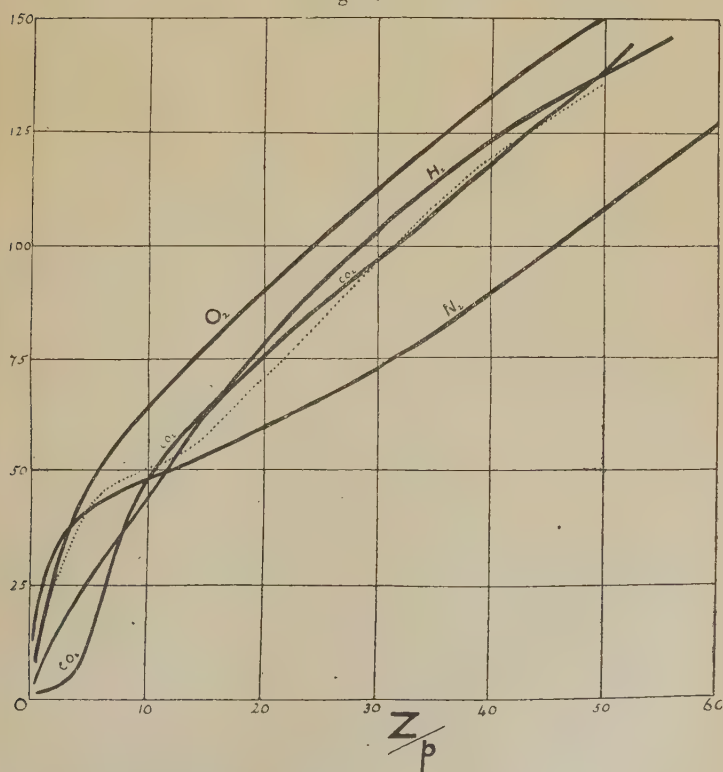
Z/p .	Z .	p .	k .	$W \cdot 10^{-5}$.
·85	4·2	4·94	11·2	20·3
1·29	6·4	4·94	15·2	24·2
1·32	4·2	2·42	17·3	25·0
2·10	6·4	3·04	24·0	31·1
2·16	10·7	4·94	24·6	31·2
3·02	14·9	4·94	34·3	35·9
3·17	6·4	2·02	35·2	36·5
3·86	19·1	4·94	40·0	39·2
3·98	6·4	1·61	40·5	40·4
3·98	14·7	3·70	40·5	40·2
4·21	12·8	3·04	41·0	40·8
4·26	8·6	2·02	41·8	41·1
4·29	21·2	4·94	41·9	40·9
4·96	6·4	1·29	45·5	42·8
5·08	18·8	3·70	47·5	43·1
5·16	25·5	4·94	49·0	43·2
5·21	12·6	2·42	48·6	43·3
6·27	23·2	3·70	53·2	46·4
6·32	19·2	3·04	53·6	46·8
6·82	33·7	4·94	53·7	47·9
7·95	12·8	1·61	59·5	53·1
8·42	25·6	3·04	58·9	54·4
13·7	12·9	·94	70·9	73·1
14·1	42·7	3·04	73·4	74·9
17·1	16·7	·98	84·3	86·7
17·6	42·5	2·42	84·2	85·7
23·5	23·2	·98	102·5	112
23·8	38·2	1·61	100	114
33·3	42·9	1·29	118	148
33·5	23·3	·695	123	148
39·9	27·7	·695	131	172
40·1	38·5	·94	133	176
46·2	32·1	·695	143	192
52·5	36·5	·695	155	215
58·6	40·7	·695	162	235

4. Another set of experiments was made with the apparatus where the electrons passed through a slit 4 cm. from the receiving electrodes, and a selection from the results obtained with this instrument is given in Table II.

TABLE II.—Oxygen.

Z/p .	Z .	p .	h .	$W \cdot 10^{-5}$.
·358	2·10	6·42	5·52	6·20
·430	2·10	4·82	6·47	10·6
·504	2·10	4·17	7·00	13·4
2·46	8·25	3·36	24·5	33·1
3·83	12·85	3·36	39·1	39·0
4·82	15·00	3·11	55·3	41·6
6·05	18·80	3·11	53·4	44·3
7·92	21·3	2·69	58·2	51·1
9·64	21·3	2·21	62·3	56·1
14·3	31·6	2·21	74·5	74·7
18·0	39·7	2·21	86·1	84·7

Fig. 1.



The results obtained with the two instruments are thus seen to be in good agreement, and may be represented by the curves given in figs. 1 and 2, in which the larger values of h and W are the ordinates and the ratio Z/p the abscissæ.

Fig. 2.

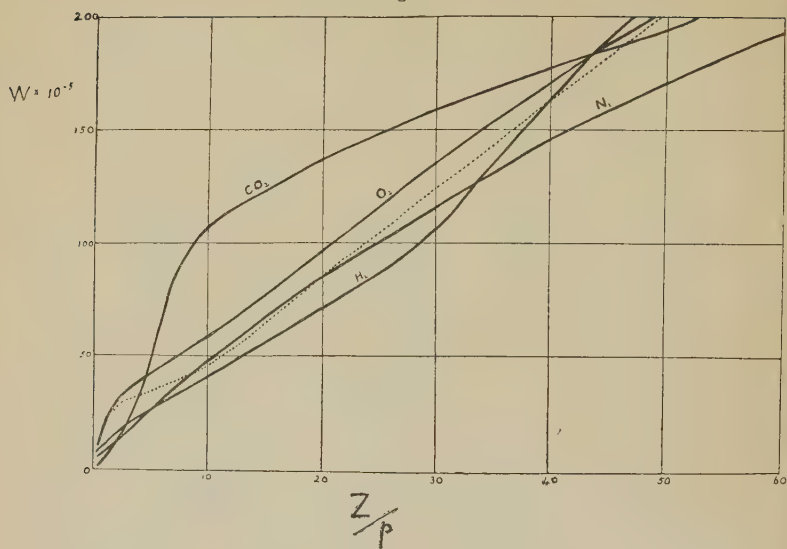
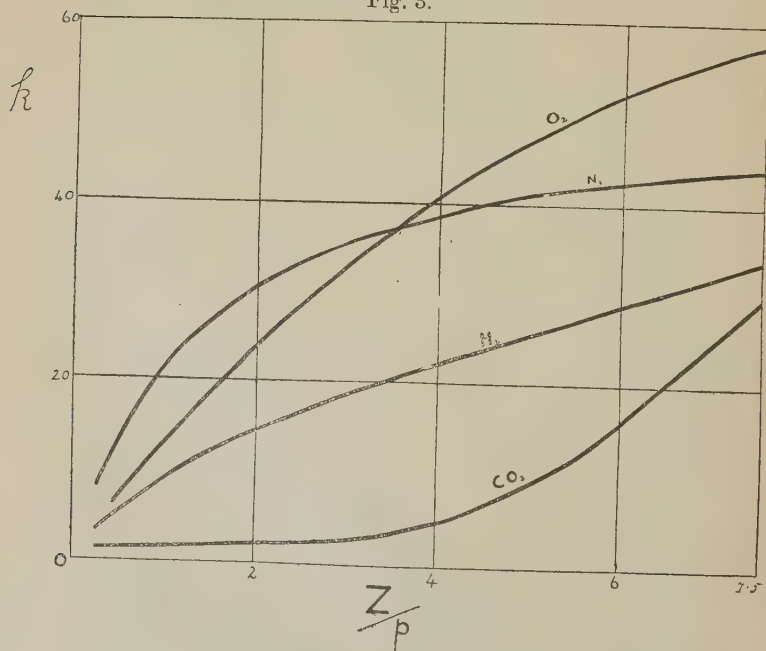
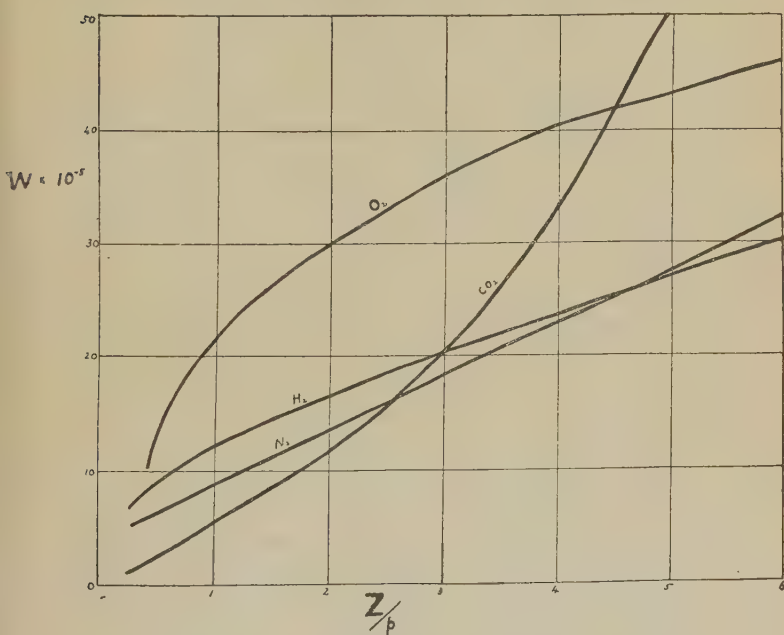


Fig. 3.



The electric force Z is expressed in volts per centimetre, the pressure p in millimetres of mercury, and the velocities W and U in centimetres per second. The smaller values of k and W are similarly represented by the curves in figs. 3 and 4.

Fig. 4.



For comparison, the corresponding curves for nitrogen, hydrogen, and carbon dioxide are also given, and the dotted curves represent the results obtained in the first experiments with the apparatus where the insulation was of ebonite. As indicated in the curves for oxygen the proportion of ions in the stream of electrons becomes smaller as the pressure decreases, for the difference between points on the dotted and continuous curves for the small value of Z/p becomes relatively less when Z is constant and p reduced.

An apparatus was also used in which the electrons were produced by a hot filament. It was first tested by making measurements with hydrogen. The results obtained with the filament are given in Table III. as k_1 and W_1 . The neighbouring columns contain the values k_2 and W_2 which had been obtained earlier by Townsend and Bailey (*loc. cit.*) with an instrument where the electrons had been produced by the action of ultra-violet light.

These results agree within the error of experiment, which is less than 5 per cent.

TABLE III.—Hydrogen.

p .	Z .	Z/p .	k_1 .	k_2 .	$W_1 \cdot 10^{-5}$.	$W_2 \cdot 10^{-5}$.
2.28	6.4	2.8	18.6	18.6	18.2	18.9
2.28	12.8	5.58	27.3	28.1	25.3	26.2
2.28	19.2	8.42	37.3	38.5	32.7	34.2
2.28	25.6	11.2	47.4	48.4	37.9	40.2
.26	12.8	49.2	142	147		
.26	19.2	73.8	192	193		

This proved that there could have been no action of the ultra-violet light which affected the measurements of U and W in hydrogen. It was found that a sufficient stream of electrons for making measurements in hydrogen with this instrument was produced when the filament was kept at a dull red glow.

When the instrument had been exhausted and washed out several times with pure oxygen, it was found that a sufficient stream of electrons was emitted in oxygen only when the filament was made to glow very brightly at a much higher temperature than in the case of hydrogen.

The velocities obtained in oxygen by using the filament as a source of electrons were generally smaller than those obtained in the earlier experiments with ultra-violet light, and were rather irregular. The results indicated that there was a number of ions in the stream which increased with the pressure. These effects were probably due to an impurity in the gas introduced by the action of the hot oxygen on wax used to make an air-tight joint near the filament.

5. The results of the experiments in which ultra-violet light was used are represented by curves (figs. 1 to 4) which exhibit the quantities k and W in terms of the ratio Z/p . The values of k and W corresponding to a series of values of the ratio Z/p are given in Table IV. The third column of the table gives the values of the velocities of agitation U of the electrons which have been calculated by means of the formula (1). The fourth column contains the corresponding values of the mean free path L obtained by the formula

$$W = \frac{ZeL}{pmU} \times .815,$$

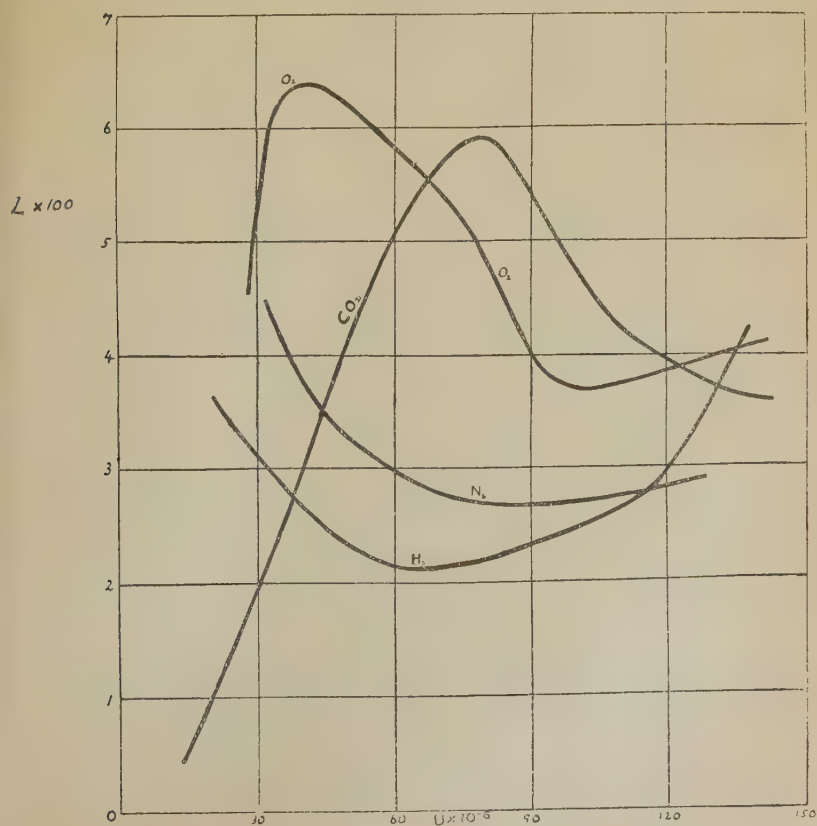
where L is the mean free path of electrons moving with the velocity of agitation U in the gas at 1 millimetre pressure. The velocities W and U are in centimetres per second, L in centimetres, Z in volts per centimetre, and p in millimetres of mercury.

The manner in which L depends on U is shown graphically in fig. 5. The curves showing the relation between these

TABLE IV.—Oxygen.

$Z/p.$	$k.$	$W. 10^{-5}.$	$U. 10^{-6}.$	$L \times 100.$	$\lambda \times 10^4.$
50	150	205	141	4.05	521
40	133	172	133	3.99	414
30	113	136	123	3.87	303
20	90	98	109	3.74	199
15	77	78	101	3.67	147
14	74	74	99	3.66	138
13	72	71	97.6	3.73	130
12	69	67	95.6	3.74	121
10	64	60	92.0	3.86	105
7	56	50	86.1	4.31	83.0
5	47	43	78.8	4.89	73.0
2	24	30	56.3	5.91	69.8
1	13	22	41.3	6.39	69.1
.8	10.8	19	37.8	6.29	62.6
.6	8.4	16	33.4	6.22	56.6
.4	6	10	28.2	4.93	27.5

Fig. 5.



quantities in the case of nitrogen, oxygen, and carbon dioxide are also given, as they have not previously been exhibited in this way.

The results for oxygen disclose the fact that, as the velocity of agitation of the electrons decreases from 14×10^7 to 10×10^7 cm. per sec., the mean free path becomes smaller and then gradually increases to nearly twice the value of its previous minimum, just as has been shown to be the case with the inert gases, in which the phenomenon is much more marked, and certain other gases to a less degree. In oxygen, however, a stage is reached when, as the velocity of agitation of the electrons decreases still further, the mean free path attains a maximum, after which it rapidly becomes smaller. A similar result was obtained by Skinker* in carbon dioxide.

Thus within a comparatively short range of velocities a maximum and a minimum value of the mean free path of electrons are obtained in oxygen. After this effect had been observed in oxygen, Skinker's experiments on carbon dioxide were repeated and his results were corroborated.

The minimum mean free path .0366 cm. is obtained with the velocity 10^8 cm. per sec., which is the velocity acquired by the electron in moving in a field of 2.7 volts, and the maximum mean free path .064 cm. is obtained with the velocity $4.1 \cdot 10^7$ cm. per sec. corresponding to .48 volt.

6. The sixth column of Table IV. contains the values of the fraction λ of the mean energy of agitation $\frac{mU^2}{2}$, which is lost by an electron in a collision with a molecule of oxygen. These values were obtained from the formula:

$$\lambda = 2.46 \cdot \frac{W^2}{U^2} \cdot \cdot \cdot \cdot \cdot \cdot (3)$$

It is seen that λ increases with U . Some of the loss of energy in the collisions with the smaller velocities is probably due to dissociation of the molecules. This effect would occur before ionization by collision, as is seen from Kirkby's† experiments, which show that with small values of the ratio Z/p the number of molecules of oxygen which are dissociated exceeds the number ionized by collision.

7. The oxygen used in the above experiments was prepared by the electrolysis of a saturated solution of pure

* M. F. Skinker, *Phil. Mag.* xliv. p. 924 (1922).

† P. J. Kirkby, *Phil. Mag.* p. 559 (1908).

barium hydrate. The limbs of the electrolysis tube were so constructed that the backward diffusion of hydrogen was rendered impossible. The oxygen was dried in several stages. It was first left for a day or more in contact with pure caustic potash. It was then dried three times in succession for shorter periods in phosphorus pentoxide, and was admitted into the main apparatus through a glass tube which was internally silvered, so that when communication with the mercury pumps and the McLeod gauge was cut off by a tap, the mercury vapour was gradually absorbed by the silver. Each apparatus was exhausted to a pressure less than 3_{00}^1 mm., and was tested for air tightness over several weeks during vacation. No sign of a leak was registered on the McLeod gauge. Traces of impurity were removed by admitting oxygen to a pressure of at least 5 mm., which was pumped out to below 3_{00}^1 mm. by means of a Gaede diffusion pump. This process was repeated several times until the percentage of impurity in the apparatus could be regarded as negligible.

The hydrogen used was admitted through a palladium tube after the apparatus had been exhausted. The carbon dioxide was prepared by heating some sodium bicarbonate. The order of the currents used in these gases was 10^{-12} ampere.

8. It may be of interest to draw attention to some attempts that have been made to account for the increase of the mean free paths of electrons as the velocity diminishes. F. Hund* has worked out an electrostatic field of force surrounding an atom which is such that almost all electrons of a certain small velocity are deflected by an amount 2π , and which leads to the existence of a maximum for L . He finds, however, that the power law of attraction near the nucleus of the atom disagrees with that roughly estimated from other data, and that argon should be the only gas which exhibits so pronounced an increase of L with U . He therefore assumes that, if the electron is moving so slowly that its deflexion, as calculated on the basis of classical electrodynamics, would entail a loss of energy greater than that actually possessed by the electron in the form of kinetic energy, it simply passes through the atom, which may thus be regarded as ring-shaped, the size of the inner circle of the ring increasing as the velocity U of the electron diminishes. By applying the ideas which H. A. Kramers †

* F. Hund, *Zeits. für Phys.* xiii. p. 241 (1923).

† H. A. Kramers, *Phil. Mag.* xlv. p. 836 (1923).

used in dealing with the emission of the continuous X-ray spectrum, he infers that, when an electron travelling along a rectilinear path collides with an atom, there is a certain probability of transition to a path of less energy which is also rectilinear, but that for decreasing values of U this probability rapidly becomes very small compared with L , so that a great number of electrons do not radiate during the collision, but remain in their stationary orbits and behave as if the atoms were not present. The reasoning does not appear to lead to a satisfactory quantitative result.

A second attempt to sketch a theory for the increase of L has been undertaken by Zwicky*.

He shows that the resources of the classical theory have not been exhausted by Hund, and that it is not necessary to have recourse to quantum methods to adduce an explanation which starts from comparatively simple assumptions. Like Hund, he restricts himself to considering inert gases which have no electron affinity. He calculates the deflexion experienced by an atom in colliding with four types of an atom, which are successively closer approximations to the true atom. Even when the atoms are regarded as being polarized by the electric field and having, in addition, a quadrupole moment, no increase of L occurs. He therefore adopts as his final approximation to the true atom a rotating dipole which excites an alternating field. On account of the phase relations that arise between the velocity of the electron and the period of the vibrations in the field, an increase of L with a decrease of U (in the terminology of this paper) becomes possible. By elementary considerations Zwicky shows that an electron which approaches a highly symmetrical atom pursues an ever-widening spiral path whose diameter is of the order of that of the atom when in close proximity to it, so that the electron may pass around and beyond it and need not go through it. A more complete knowledge of L at still lower electron velocities for a number of gases will be necessary before the nature of the collisions which occur will be sufficiently clear to enable an adequate theory to be set up.

The above researches were carried out in the Electrical Laboratory, Oxford. I wish to take this opportunity of thanking Professor Townsend for his valuable advice during the course of the work.

* F. Zwicky, *Phys. Zeitschr.* xxiv. p. 171 (1923).

LVI. *Note on Saha's Ionization Formula, and on the Theoretical Value of the Photo-electric Absorption Coefficient.* By Prof. E. A. MILNE*.

CONSIDER an assembly of atoms in thermodynamic equilibrium at temperature T , whose ionization potential is χ_1 . Let x be the degree of ionization, P_e the partial pressure of free electrons. Saha's formula † for the degree of ionization, as modified by R. H. Fowler‡, is as follows:—

$$\frac{x}{1-x} P_e = \frac{(kT)^{5/2} e^{-\chi_1/kT} (2\pi m)^{3/2} \sigma}{h^3 b(T)}. \quad (1)$$

Here h is Planck's constant, k Boltzmann's constant, σ is the "symmetry number" of the atom, and $b(T)$ is the partition function of the neutral atom given by

$$b(T) = q_1 + q_2 e^{-(\chi_1 - \chi_2)/kT} + q_3 e^{-(\chi_1 - \chi_3)/kT} + \dots, \quad (2)$$

where χ_2, χ_3, \dots denote the energy-levels of the possible excited states of the neutral atom, and q_1, q_2, q_3, \dots are the *a priori* weights of the normal and the several excited states. It is assumed that no atoms are present in a higher degree of ionization. In this form the formula was cited by Fowler and Milne §, and it has been frequently re-quoted from the latter paper.

Unfortunately, as it stands (1) is not in general correct. It becomes correct on inserting a factor $b'(T)$ in the numerator on the right-hand side, where $b'(T)$ is the partition function for the ionized atom, and is given by a formula analogous to (2).

Formula (1) is correct in the case when $b'(T)=1$. Herein is the origin of the error. The corrected version is given in general terms in equation (9.94) of Fowler's original paper, but his investigation is usually explicitly confined to the case in which the ionized atom possesses no energy other than translational, *i. e.* to the case $b'(T)=1$. This is in fact true for ionized hydrogen, which Fowler considered in detail ||.

It is now easily seen that the appearance of the factors

* Communicated by the Author.

† Phil. Mag. xl. p. 479 (1920). ‡ Phil. Mag. xlv. p. 21 (1923).

§ Monthly Notices, R. A. S. lxxxiii. p. 407 (1923).

|| *Loc. cit.* section 7.

$b(T)$ and $b'(T)$ is really an unnecessary complication; they disappear if we compare the numbers of ionized and neutral atoms in their normal states, instead of the whole numbers of ionized and neutral atoms. If n', n are the former numbers, q', q the weights of the normal states of the ionized and neutral atom, we have simply

$$\frac{n'}{n} P_e = \frac{q'}{q} (kT)^{5/2} e^{-\chi_1/kT} \frac{(2\pi m)^{3/2} \sigma}{h^3}. \quad \dots \quad (3)$$

If N', N are the total numbers of ionized and neutral atoms,

$$N' = \frac{n'b'(T)}{q'}, \quad N = \frac{nb(T)}{q},$$

and the degree of ionization is given by

$$x = \frac{N'}{N + N'}, \quad 1 - x = \frac{N}{N + N'},$$

and thus

$$\frac{x}{1-x} P_e = \frac{b'(T)}{b(T)} (kT)^{5/2} e^{-\chi_1/kT} \frac{(2\pi m)^{3/2} \sigma}{h^3}. \quad \dots \quad (4)$$

When the weights of the lowest state of the ionized and neutral atom are unequal, the correction will make an appreciable difference to the calculated degree of ionization. But I wish here principally to point out an important consequence of the correction, namely that it implies a correction to the formula for the coefficient of absorption of an atom beyond a series limit*, as given independently by Kramers† and the writer‡.

The formula in question was deduced by the writer by equating the number of photo-electric ejections of electrons to the number of captures of electrons by ionized atoms. Let $\psi_r(\nu) I_\nu d\nu dt$ be the probability that a neutral atom in a state r of weight q_r will in time dt , under the influence of isotropic ν -radiation of intensity $I_\nu d\nu$, become ionized by

* The correction is of importance in the calculation of the general coefficients of absorption of an ionized gas: the writer has made this calculation, with the corrected formula, in Monthly Notices, R. A. S. lxxxv. June 1925.

† Phil. Mag. xlv. p. 843 (1923).

‡ Phil. Mag. xlvii. p. 224 (1924). The same formula was also arrived at independently by Becker, but explicitly confined to the case of hydrogen, where the correction makes no difference (*Zeits. für Phys.* xviii. p. 333, 1923).

absorption of a quantum of energy $h\nu$, with the emission of an electron of speed v given by

$$h\nu = \frac{1}{2}mv^2 + \chi_r, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where χ_r is the ionization potential in the r -state. The coefficient $\psi_r(\nu)$ is an Einstein probability coefficient, and is connected with the atomic absorption coefficient $\alpha_r(\nu)$ by the relation

$$\alpha_r(\nu) = \frac{h\nu\psi_r(\nu)}{4\pi}.$$

Further, let n_r be the number of atoms per unit volume in the r -state, n the number of ionized atoms in their lowest state, n_e the number of free electrons.

An application of the principle of detailed balancing of elementary processes (in this case, ejections and captures) then shows that

$$\begin{aligned} n_r\psi_r(\nu)I_\nu dv dt \\ = 8\pi^2 n' n_e \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{1}{2}mv^2/kT} [F_r(\nu) + I_\nu G_r(\nu)] v^3 dv dt, \end{aligned} \quad . \quad . \quad . \quad (6)$$

where $2\pi F_r(\nu)$ is the probability* of the unstimulated capture of a v -electron in the r -orbit by the ionized atom in its neutral state, and $2\pi I_\nu G_r(\nu)$ is the similar probability of a stimulated capture.

We now eliminate n'/n_r by the ionization equation

$$\frac{n'}{n_r} P_e = \frac{q'}{q_r} (kT)^{5/2} e^{-\chi_r/kT} \frac{(2\pi m)^{3/2} \sigma}{h^3}, \quad . \quad . \quad . \quad (7)$$

and substitute Planck's formula for I_ν . On applying (5), and imposing the condition that $\psi_r(\nu)$, $F_r(\nu)$, $G_r(\nu)$ must be independent of the temperature, we arrive at the formula

$$\alpha_r(\nu) = \frac{h\nu\psi_r(\nu)}{4\pi} = \frac{q'm^2\sigma}{2q_r} \cdot \left(\frac{c}{h\nu} \right)^2 2\pi F_r(\nu). \quad . \quad . \quad (8)$$

This differs from the formula previously given by the writer and from the formula derived by a somewhat different method by Kramers, by the factor q' in the numerator for the weight of the normal state of the ionized atom†. It should be mentioned that the less rigorous method used by Kramers lends itself only with difficulty to the making

* More strictly, the effective cross-section of the atom for captures of the kind in question.

† The form of (8), taking account of relativity mechanics, is in effect given by Dirac, Proc. Roy. Soc. cvi. A. p. 581 (1924).

of the correction; but Kramers's own application of the formula is unaffected, as he used it for the case in which the system after ionization is a bare nucleus, for which $q' = 1$.

If it is possible for the collision of an electron with an *excited* ionized atom to result in capture in the r -orbit, then conversely it must be possible for an atom in the r -state to become ionized by the absorption of a quantum of radiation sufficiently large to leave the atom excited. The corresponding contribution to the atomic absorption coefficient would be given by (8) on introducing an appropriate value for q' , namely the weight of the excited state of the ionized atom. But the capture-probability factor $F(v)$ would probably be very small.

Summary.

Saha's formula for high-temperature ionization requires a factor (partition function) relating to the *a priori* weights of the stationary states of the ionized atom, as well as the factor relating to those of the neutral atom introduced by Fowler. The formula for the photo-electric absorption coefficient requires similarly a factor for the weight of the lowest state of the ionized atom, as well as the factor for the weight of the neutral atom given by Kramers, Becker, and the writer. In all cases a ratio of weights is necessarily involved.

[ADDENDUM.—Kramers's deduction of formula (8) depends on considering an enclosure containing a single neutral atom and calculating the ratio of the probability that the atom is in its normal state to the probability that a given electron is missing and moving free with a given velocity. Apart from the difficulty of justifying the applicability of probability considerations to a single atom in this way, it is clear that the weight of the appropriate state of the ionized atom would make an appearance in the final formula, provided we compared the probability that the atom is neutral and in a given state with the probability that the same atom is ionized and in a given state; the ratio of the weights would then necessarily occur. In the more rigorous statistical discussion, the partial pressure of the free electrons has been shown in fact to be irrelevant*, and this suggests that Kramers's method of considering the free electron is not justifiable.

Trinity College, Cambridge,
May 1925.

* Phil. Mag. xlvii. p. 225 (1924).

LVII. *Reply to Mr. U. Doi's "New Discussion of Bucherer's Experiment."* By A. H. BUCHERER, *Doctor of Science, Professor of Theoretical Physics* *.

IN this Magazine Mr. U. Doi has published a new discussion of the experiments carried out by me for the purpose of ascertaining the law of mass variability. The aim of Mr. Doi has been to establish an agreement between my experimental results and a formula of his own, which he derives from his anti-Einsteinian theory of relativity. He finds for the specific charge of the electron :

$$\frac{e}{m} = \frac{e(1-\beta^2)}{m_0}, \quad (1)$$

while my experiments prove the Lorentz formula :

$$\frac{e}{m} = e \frac{\sqrt{1-\beta^2}}{m_0}, \quad (2)$$

where, as usual, β signifies the ratio of the velocity of the electron to that of light.

The latter formula has subsequently been confirmed by other investigators. I refer to the work of my assistant, Mr. K. Wolz, to that of Neumann and of Cl. Schaefer, of E. Hupka and of Ch. Guye. It seems to me there cannot be a reasonable doubt as to its correctness. According to my original plan, one single radiographic curve should have sufficed to establish the law of mass variability. But it turned out that the trace of the curve at points of small deflexions resulted from two superimposed effects, the one being the radiographic action of the β -rays on which the forces acting between the condenser plates were balanced, and the other where they were not balanced.

Now the original theory of the experiment referred to the compensated rays corresponding to large deflexions ; and as the theory of the non-compensated rays appeared at that time intricate and difficult, I decided to produce a number of radiographic curves whose maxima were so calculated as to represent varying velocities of the electrons. Only these maxima were measured, and from them the mass variability was deduced with the assistance of the constants of the apparatus and of the electromagnetic data.

* Phil. Mag. xlix. p. 434 (1925).

Recently Mr. T. Lewis * has developed the complete theory of the curve, taking in account all factors that condition the trace. In future, then, it will be possible to demonstrate the validity of the Lorentz mass formula from a single radiogram. Unfortunately, the experimental films I could place at Mr. T. Lewis's disposal were too scanty, and in consequence the Lorentz formula could only be established up to velocities of $\beta = 0.8$.

Comparing Mr. Doi's interpretation of the curve with that of Mr. Lewis, it becomes evident at once that the former by neglecting the most important factors at work in producing the trace cannot be accepted as proving any mass formula. I refer the reader to Mr. Lewis's exceedingly interesting paper.

It may not be superfluous to state that today the confirmation of the Lorentz formula can no longer be adduced as proving the Einsteinian theory of relativity. As Mr. P. Lenard has shown, this mass formula results from a very simple application of mechanics. For, putting for the total energy E of a mass m the expression which Hasenöhrle derived from the Maxwellian theory,

$$E = mc^2,$$

where c signifies the velocity of light; and equating this change of energy in unit time to the change of kinetic energy of the mass moving with velocity v , we obtain at once

$$\frac{dE}{dt} = \frac{vd(mv)}{dt}.$$

$$\therefore m = \frac{m_0}{\sqrt{1-\beta^2}}.$$

Mr. Doi in concluding his paper proposes a value for the specific charge of the electron $\frac{e}{m_0}$ obtained by Prof. A. Sommerfeld by applying the special theory of relativity to the spectroscopy of hydrogen and helium. However, this application to the motion of the electrons within the atom is certainly not permissible, and the agreement between his theory and the spectroscopic data is only apparent.

Bonn, June 6th, 1925.

* Thos. Lewis, B.Sc., Proc. Roy. Soc. A. vol. cvii. pp. 544-560.

LVIII. *On the Transmission of Air-Waves through Pipes.*
 By L. F. G. SIMMONS, B.A., A.R.C.Sc., and F. C.
 JOHANSEN, B.Sc., of the Aerodynamics Department,
 National Physical Laboratory*.

INTRODUCTION.

THE technique of air-speed measurement by means of pressure tubes has received considerable attention in recent years, and with the sensitive pressure gauges now available no difficulty is experienced in determining, to a high degree of accuracy, the speed of steady air-currents. In studying unsteady currents, such as natural winds, continuous records may be obtained by connecting the open ends of the pressure tubes to opposite sides of a specially constructed diaphragm gauge made with light moving parts and possessing a high natural frequency. But these records may fail to indicate the actual pressure changes which occur at the open ends on account of the wave-motions induced in the tubes being influenced by the viscosity of the air and by the volume of air enclosed in the gauge. Both factors exert a sensible influence on the results, and where long pipes of small diameters are employed they may lead to serious errors in the estimation of wind speed.

Some idea of the magnitude of the errors involved in certain simple cases representative of gusts and periodic flow is provided from experiments recently conducted at the National Physical Laboratory on the transmission of waves through rubber pipes. Grouped under two headings, the experiments deal (1) with the propagation of a single wave resulting from the sudden application of a known pressure at one end of the pipe, and (2) with waves generated by simple harmonic variations of pressure or displacement, applied at one end. The results pertaining to closed pipes indicate the relationship existing between the pressures at any instant at the two ends, and the extent to which these are affected by size and length of pipe, and by the type of gauge used; whilst measurements of the displacement made at the end of open pipes may be compared with calculations based on the theory given by Lord Rayleigh. This theory (which was propounded in relation to acoustic problems) is of course subject to the usual limitations: (1) that the maximum velocity must

* Communicated by Mr. R. V. Southwell, F.R.S.

be small compared with the velocity of sound, (2) that $\frac{VD}{v}$ must not exceed a certain limit. Uniform motion across each section is presupposed, except within a thin boundary layer in the immediate neighbourhood of the wall, and this assumption imposes a further limitation upon the theory, restricting its application to pipes larger than a certain minimum diameter; for when the thickness of the boundary layer becomes comparable with the diameter the distribution across the section cannot remain uniform. There is reason to believe that the conditions assumed are realized in the experiments made with pipes of .475 cm. and .950 cm. diameter; hence any comparison between experimental and theoretical results is valuable, not only in showing the deficiencies of the existing theory, but also as a basis of reference for checking future theories.

A rough survey of the results shows that (except where resonance occurs, as with pipes of .95 cm. diameter) the transmitted pressure is less than that applied, and is subject to a lag in phase which delays the reception of the wave at the far end. As a general rule it may be taken that a reduction in the pressure amplitude, together with an increased phase lag, are produced by :

- (i.) an increase in length of pipe,
- (ii.) a decrease in diameter,
- (iii.) an increase in frequency.

Where comparisons have been made, large discrepancies exist between the experimental and calculated values. In some cases the comparisons are perhaps hardly legitimate, since the end conditions required for a simple solution of the equations of motion were only approximately fulfilled by the apparatus employed; but in other cases, where no doubts of this nature exist, the evidence shows that the present experiments do not fall within the range of applicability of Rayleigh's theory. Lastly, the experiments demonstrate the unsuitability of the ordinary type of diaphragm gauge for recording, in detail, rapidly changing pressures such as occur during rapid manoeuvres of aircraft, or in natural winds during gusty weather, and point to the need of a new form of gauge of small internal volume.

The present communication is divided for convenience into three parts. The first is devoted to a review of the Rayleigh theory of wave-motion through pipes; the second deals with experiments in which pressures were measured

with a diaphragm gauge; and the third with later experiments in which more refined means of measuring pressure and displacement were introduced.

PART I.—REVIEW OF THEORY.

Apart from the results of a few rough experiments, no data appear to be available relating to the effects of viscosity on the transmission of air-waves through pipes. On the theoretical side, the subject has received some attention from a number of physicists—notably Stokes, Kirchhoff, and Rayleigh,—but there is no experimental verification, as far as the writers are aware, of their calculations for the wave-motion produced by simple harmonic variation of the pressure or the displacement at one end of a pipe.

Rayleigh's elementary theory of wave propagation along a pipe is based on the assumption that the motion is wholly longitudinal and approximately uniform across any section, except near the wall where viscosity exercises a sensible influence. On the ground that the boundary layer so affected is small in comparison with the diameter of the pipe, he concludes that the viscosity forces may be calculated from Stokes's formula for the drag of an infinite plate when executing harmonic vibrations in a plane parallel to its own. The equation of motion for waves of frequency n , established in the usual manner from considerations of the forces acting on a small element of the fluid contained between two sections δx apart, is shown to be

$$\left(1 + \frac{P}{S} \sqrt{\frac{\nu}{2n}}\right) \frac{\partial^2 \xi}{\partial t^2} + \frac{P}{S} \sqrt{\frac{\nu n}{2}} \frac{\partial \xi}{\partial t} = a^2 \frac{\partial^2 \xi}{\partial x^2}, \quad (1)$$

where ξ denotes the displacement of the fluid at section x ,

ν is the coefficient of kinematic viscosity,

P = perimeter, and S = cross-sectional area of pipe.

$a = \sqrt{\frac{p_0 \gamma}{\rho_0}}$ = velocity of sound in air,

γ = ratio of specific heats of air.

* Rayleigh's 'Sound,' vol. ii. 1896 edition, p. 318. The equation given by Rayleigh has been slightly modified by the substitution of ξ for $\frac{X}{S}$.

A solution of (1) may be obtained in the form

$$\xi = \Sigma A e^{int \pm mx}, \quad \dots \quad (2)$$

provided that

$$a^2 m^2 = - \left(1 + \sqrt{\frac{\nu}{2n}} \cdot \frac{P}{S} \right) n^2 + i \sqrt{\frac{\nu n}{2}} \cdot \frac{P}{S} n, \quad \dots \quad (3)$$

where the two roots of m may be written $\pm (p + iq)$.

Making this substitution in (2), we have

$$\xi = \Sigma A e^{int \pm (p + iq)x}, \quad \dots \quad (4)$$

A particular form of this solution, applicable to the present problem (since it represents the combined effects of the incident and reflected waves) is

$$\begin{aligned} \xi = & A e^{-px} \sin (nt - qx) + B e^{-p(2l-x)} \sin \{nt - q(2l-x)\} \\ & + C e^{-px} \cos (nt - qx) + D e^{-p(2l-x)} \cos \{nt - q(2l-x)\}, \end{aligned} \quad (5)$$

where A, B, C, and D are arbitrary constants to be determined from the specified terminal conditions, and l = total length of pipe. With the aid of the relation

$$p - p_0 = -p_0 \gamma \frac{\partial \xi}{\partial x},$$

equation (5) can be used to calculate the pressure at any point in excess of the normal pressure p_0 .

On the assumption that $\xi = \xi_0 \sin nt$ at $x=0$, two cases of immediate interest arise:—

CASE 1. *Free End*.—The condition to be satisfied at $x=l$ is $\frac{\partial \xi}{\partial x} = 0$. Hence we have

$$A = B, \quad \text{and} \quad C = D;$$

$$\begin{aligned} \therefore \xi = & A e^{-px} \sin (nt - qx) + A e^{-p(2l-x)} \sin \{nt - q(2l-x)\} \\ & + C e^{-px} \cos (nt - qx) + C e^{-p(2l-x)} \cos \{nt - q(2l-x)\}, \end{aligned} \quad (6)$$

where A and C are determined by substituting $\xi = \xi_0 \sin nt$ for $x=0$ in (6), and afterwards equating coefficients of $\sin nt$ and $\cos nt$.

CASE 2. *Fixed End*.—The condition for a fixed end is

$$\xi = 0 \quad \text{at} \quad x = l.$$

We now have

$$A = -B, \quad \text{and} \quad C = -D;$$

$$\begin{aligned} \therefore \xi = & A e^{-px} \sin (nt - qx) - A e^{-p(2l-x)} \sin \{nt - q(2l-x)\} \\ & + C e^{-px} \cos (nt - qx) - C e^{-p(2l-x)} \cos \{nt - q(2l-x)\}, \end{aligned} \quad (7)$$

where, as before, A and C are determined from the condition

$$\xi = \xi_0 \sin nt \quad \text{at} \quad x = 0.$$

Again, substituting $\frac{\partial \xi}{\partial x}$ from (7) in the relation

$$p - p_0 = -p_0 \gamma \frac{\partial \xi}{\partial x},$$

we obtain the following expression for the excess pressure at the fixed end :

$$p - p_0 = 2\xi_0 e^{-pl} \gamma p_0 \sqrt{\frac{p^2 + q^2}{(1 - 2e^{-pl} \cos 2ql + e^{-4pl})}} \sin (nt - ql + \theta),$$

. . . (8)

where

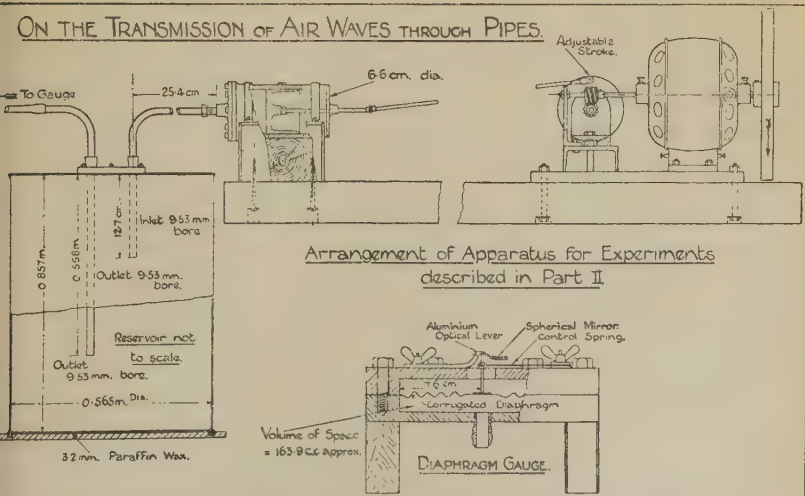
$$\tan \theta = \frac{e^{-2pl}(p \sin 2ql + q \cos 2ql) - q}{e^{-2pl}(p \cos 2ql - q \sin 2ql) - p}.$$

PART II.—MEASUREMENTS OF PRESSURE BY MEANS OF A DIAPHRAGM GAUGE.

(a) Experiments on the Propagation of Single Waves.

A preliminary series of experiments was conducted with the object of determining the influence of viscosity on the

Fig. 1.



propagation of a wave along a pipe due to a pressure suddenly applied at one end. The essential features of the apparatus comprised an air-tight reservoir of about 50 litres capacity connected by rubber pipe to the diaphragm gauge illustrated in fig. 1. A second connexion to the reservoir,

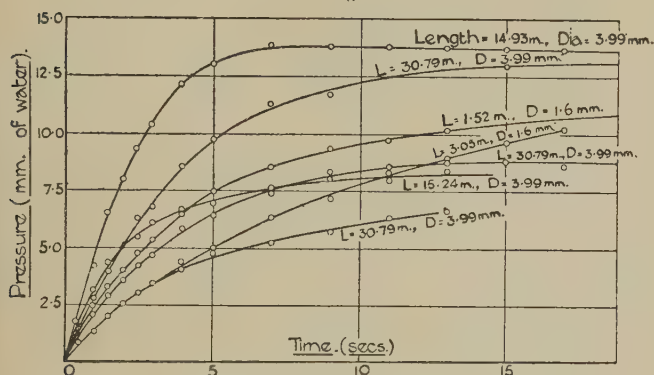
closed with a cock, enabled the pressure of the contained air to be raised to a pre-determined amount above atmospheric, usually not greater than 2 cm. of water. The gauge consisted of a chamber having a volume of about 160 c.c. closed by a corrugated metal diaphragm. A flat adjustable spring provided an additional control and enabled the sensitivity to be varied within certain limits. The motion of the diaphragm was indicated by an optical lever, made with light moving parts so as to reduce the inertia effects to a minimum, and designed to give an angular movement of the mirror proportional to the vertical displacement of the diaphragm over a range of ± 1.3 cm. of water. The natural frequency of the instrument was much higher than the frequencies common to the experiments, and the inertia effects, even in the extreme case of a sudden application of pressure to a short length of pipe, were shown to be negligible.

Observations of the deflexion of the gauge were made photographically by means of a roll-film camera operated by an electric motor, the time-scale being provided by the movement of a shutter, electrically actuated by a Weston relay, which interrupted a beam of light at uniform intervals during the unrolling of the film. In making an experiment the pressure in the reservoir was raised by admitting air at higher pressure through the by-pass into the reservoir, the gauge connexion being meanwhile stopped at the reservoir end. The film was then started, and the reservoir put into rapid communication with the gauge by means of a quick-release device.

The results of these preliminary experiments are presented in fig. 2 as curves of pressure on a time base, supplemented by Table I., which shows the time-intervals required by the pressure at the far end to reach 90 per cent. of its maximum value. They illustrate in a striking manner the influence of viscosity in delaying the growth of pressure at the far end. This final pressure is approached asymptotically, and the time-interval required depends upon the diameter and the length of the pipe; it is found to be independent of the magnitude of the pressure itself, as would be expected in the light of dimensional theory. Thus, referring to the accompanying Table I. (in which the times taken for the pressure to reach 90 per cent. of the maximum value are taken as a standard of comparison), we see that an increase in the diameter from 3.99 to 6.35 mm. reduces the time-interval from 7.8 to 1.05 secs.; a decrease in length from 30.79 to 15.24 m. is accompanied by a reduction in time from 8.2 to 6.1 secs.; but an alteration

in the initial pressure from 8.76 to 12.95 mm. of water produces no appreciable change in the time. It should be stated that the figures refer to time measured from the instant of reception of the wave at the far end (that is to say, the instant at which the diaphragm starts to

Fig. 2.



Experimental Results illustrating the Growth of Pressure at the far end of a pipe due to the sudden application of pressure at the near end.

record); there is necessarily an interval between starting and receiving the wave, but this is small, since the measurements indicated that the velocity of propagation in the smallest pipe was probably not less than 91 m./sec.

TABLE I.

Length (metres).	Pipe Int. Diameter (mm.).	Applied Pressure (mm. of water).	Time (seconds).
30.79	3.99	11.77	7.8
31.70	6.35	11.77	1.05
30.79	3.99	8.76	8.2
30.79	3.99	12.95	8.4
15.24	3.99	8.25	6.1

(b) *Waves produced by a simple harmonic pressure variation.*

The apparatus employed for the second series of experiments is illustrated in fig. 1. It consisted of an airtight reservoir of about 215 litres capacity, connected

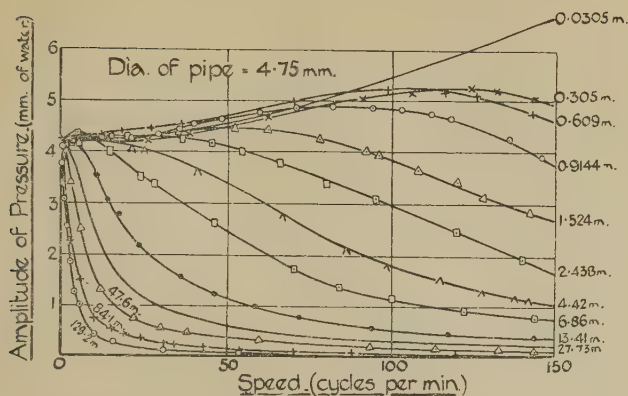
by the rubber pipe under experiment to the diaphragm gauge. The oscillating movement of a piston in a cylinder connected to the reservoir alternately compressed and expanded the enclosed air. Both the amplitude and the frequency of the pressure changes could be readily varied, but in general the pressure variation was restricted to the range ± 1 cm. of water at frequencies below 2.5 per second, the mean pressure throughout remaining atmospheric.

Measurements of transmitted pressure were made by observing the motion of a beam of light, reflected from an optical lever on the gauge to a scale placed about 4.5 metres away. To obviate errors arising from irregular movements of the zero (due either to barometric or temperature changes) the complete traverse of the spot of light from side to side was noted, and the mean value of a large number of oscillations was accepted as representing the maximum range of pressure for the frequency under investigation. From observations of the position of the reflected beam at the instant when the piston reached one end of the stroke, rough estimates were made of the phase-displacement between the forcing motion and the pressure at the gauge; these measurements were greatly facilitated by the use of a second beam of light actuated by an electric contact fixed to the piston rod in such a position that the light became visible as a flash on the scale when the piston reached its extreme position.

This series of experiments provides measurements of the pressure at the far end of rubber pipes up to 122 metres in length produced by a harmonic variation of imposed pressure. Details of the amplitude and phase relationships existing between the transmitted and impressed values are afforded by the curves of figs. 3 and 4, which refer to pipes of 4.75 mm. and 9.53 mm. bore respectively. It should be mentioned that the figures indicating the length of pipe refer in all cases to the length, including that of a short reduction piece, beyond the outlet pipe from the reservoir.

An examination of these curves reveals several important features: in the first place it is seen that, for a given frequency, the amplitude of the transmitted pressure is in general smaller than that of the applied pressure; and, in the second, that the transmitted pressure is diminished by a reduction of pipe diameter, as is evident from a comparison of the curves of figs. 3 and 4. Further, fig. 4 clearly indicates the occurrence of resonance in pipes of 9.53 mm. diameter, and shows the influence of pipe-length

Fig. 3.



Variation of Transmitted Pressure with Frequency
for pipes of various lengths due to a simple
harmonic pressure applied at the near end.

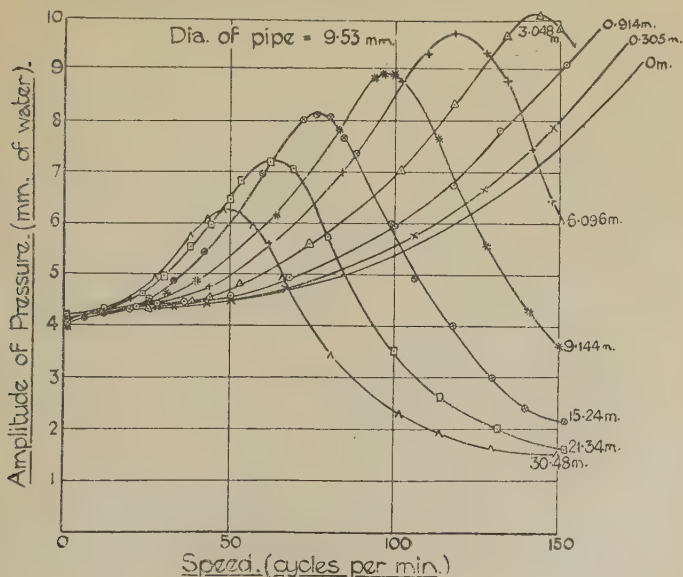


Fig. 4.

in modifying the maximum amplitude. From a consideration of fig. 4 it is apparent that even with the shortest pipe—viz., the outlet pipe from the reservoir (about 0.813 m. long and 9.53 mm. bore)—the rise of transmitted pressure

with an increase in the speed of fluctuation indicates an approach to a condition of resonance: on this account an allowance must be made for the presence of the outlet pipe in any comparison undertaken between the different results. The curve designated 0 m. in fig. 4 has been taken (for purposes of calculation) to represent the standard pressure at the near end of the pipe for different frequencies. From a few experiments, the results of which are not here included, a lag in phase was observed between the impressed and transmitted pressures. This phase displacement was found to increase in magnitude with an increase in the length and a decrease in the diameter of the pipe.

Comparison with Theory.—In a number of cases, values for the pressures have been calculated by the use of Rayleigh's formula (see Part I.), and these, together with the corresponding observed values, are given in the following Table:—

TABLE II.

Frequency (cycles per minute).	Pipe.		Pressure (mm. of water).	
	Internal Diameter (mm.).	Length (metres).	Calculated.	Observed.
50	1.6	0.76	4.57	0.56
50	1.6	2.59	4.54	0.13
50	3.175	6.10	4.62	1.17
50	3.175	24.38	5.48	0.25
50	4.75	6.10	4.59	2.43
50	4.75	24.38	5.28	0.64
50	9.53	6.10	4.59	4.93
50	9.53	24.38	5.08	6.55

Note.—In all calculations a value of 0.144 in c.g.s. units has been taken for the kinematic viscosity of air.

The discrepancies existing between calculated and observed values are too large to admit of any useful comparison being made between the two sets, and suggest the desirability of investigating the terminal conditions existing in the pipe.

An estimate of the compression of the air in the gauge caused by a pressure of about the magnitude met with in the experiments shows that there is an appreciable movement of air at the far end of the pipe. The assumption, therefore,

that the gauge constitutes a fixed end is useful only for purposes of rough comparison. An attempt was made to calculate the effect of the motion of the air into the gauge on the recorded pressure, but although the correction from this cause was found to be so large as to indicate the importance of making a similar allowance in all cases where fluctuating pressures are measured by means of a diaphragm gauge, it cannot account for the wide divergence between the calculated and observed results.

The same conclusion can be drawn with regard to a correction for the conditions obtaining at the near end of the pipe. Further, the difficulty of estimating with any certainty the complex behaviour of the air in the reservoir makes it advisable to conduct experiments with a modified form of apparatus rather than to introduce a further correction factor which will probably account for no more than a small proportion of the discrepancy. A consideration of these experiments furnishes the subject matter of Part III.

PART III.—MEASUREMENTS OF PRESSURE BY MEANS OF ALCOHOL MANOMETERS.

In order to obviate the difficulties inherent in the use of the reservoir and diaphragm gauge, modifications were made in the apparatus so as to secure conditions at the ends of the pipe under experiment capable of mathematical expression, to as close an approximation as possible. The reservoir at the near end of the pipe was dispensed with, the experimental pipe of 9.53 mm. diameter being directly connected to a cylinder of the same bore. By means of a piston and crank mechanism, a definite simple harmonic displacement of the air could be secured at the near end: the amplitude could be readily varied within fairly wide limits, but most of the measurements were obtained with a piston-stroke of 29 mm.

Of the several attempts to measure pressure whilst maintaining approximately zero displacement of the air at the far end of the pipe, the most successful involved the use of a liquid manometer consisting of a glass tube of small diameter (about 2 mm.) supported vertically with its lower end below the free surface of alcohol contained in a vessel of much greater diameter (about 25 mm.). Reliable results were obtained with this type of gauge at the lower speeds, but at higher speeds the readings were influenced by the inertia and viscosity of the alcohol.

To calculate the corrections required, it is necessary to suppose that the column of liquid oscillates through a small range $\pm a$ about a mean position distant l from the end, under the action of an applied pressure $p \sin nt$. On the reasonable assumptions that the resulting force due to surface tension remains unchanged and that the mass of oscillating liquid is constant, the equation of motion is easily seen to be

$$\rho(l+a)\frac{d^2x}{dt^2} + k(l+a)\frac{dx}{dt} + g\rho x = p \sin nt,$$

where the first two terms represent the relatively small forces due to inertia and viscosity respectively: thus p can be determined from the known solution of the equation. Clearly, this method leads only to an approximate estimate of the corrections; hence the numerical results given for pressures at the higher speeds do not represent the same degree of accuracy as those at the lower speeds.

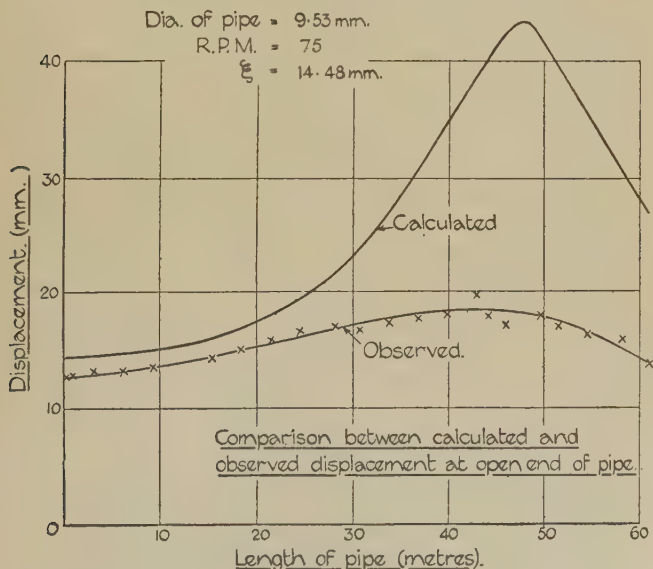
The coefficient of viscosity, k , appropriate to the motion was determined from oscillation experiments with a U-tube partly filled with alcohol: a value of 35 c.g.s. units found from these experiments has been taken for the purpose of the calculations.

Open-ended pipes.—The displacement of the air at the open end was made apparent by the motion of a soap-film introduced into a glass tube, about 20 cm. in length and about 12.7 mm. in diameter, connected to the end of the pipe. When at rest, the film formed a thin diaphragm across a section about half-way along the tube; during an experiment it oscillated about this position with an amplitude which in some cases approached 5 cm. To obtain satisfactory results it was found necessary to keep the wall of the tube wet with the soap solution: this reduced the resistance to motion and at the same time tended to preserve the existence of the film, which generally lasted for less than a minute. With precautions taken to secure the best conditions, the maximum resistance at the highest speeds was less than a pressure of 1.25 mm. of water: in other words, the far end did not accurately conform to the conditions of a free end owing to the existence of this extraneous pressure. Rough calculations show, however, that the maximum error from this cause is probably less than 6 per cent. of the observed value of the displacement. It should be added that the dis-

placements could be measured in the majority of cases to within 0.5 mm. (*i.e.* about 1 per cent.), and that the film results were subsequently checked by observing the motion of smoke injected into the tube.

Fig. 5 shows the variation of amplitude with length of pipe at a constant speed (R.P.M. = 75) resulting from a forced motion ($\xi = 14.5 \sin 7.85t$) imposed at the near end. Theory and experiments indicate a critical length of pipe (in the neighbourhood of 46 metres) at which the dis-

Fig. 5.



placement reaches a maximum; but whereas the observed value of this displacement is 19 mm., the figure calculated from equation 6 (p. 556) is 44.4 mm. This difference is not likely to be materially reduced if an allowance is made for the pressure required to overcome the resistance opposing the motion of the film, since in the particular case ($l=0$) the difference from this cause is only about 10 per cent. of the observed value. Further evidence of the want of concordance between the two sets is seen in the accompanying Table of results pertaining to a pipe of length 30.5 metres and 9.53 mm. diameter.

TABLE III.

Amplitude of Displacement (mm.) at
far end of 30.48 metres pipe.

R.P.M.	Calculated.	Observed.
25	15.24	14.47
75	21.2	19.55
115	33.78	26.42 (max.)
155	82.55 (max.)	15.49
180	38.61	—

These figures are of interest in showing that both the calculated and observed values for the displacement increase with frequency up to a certain point where a maximum

Fig. 6.

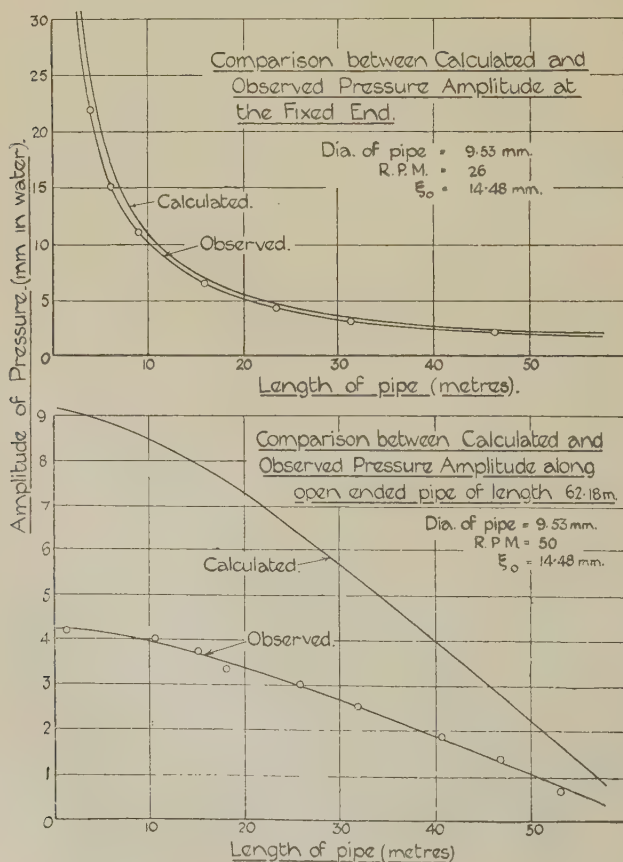


Fig. 7.

value is reached. In contrast, however, with the curves of fig. 5, where the observed and calculated maxima are seen to occur at about the same lengths of pipe, the maxima here occur at widely different frequencies.

In figs. 6 and 7 amplitude of pressure is plotted against length of 9.53 mm. bore pipe for the two conditions of fixed and open end respectively. The pressure was measured at the end of the closed pipe, and at intermediate points along the open-ended pipe. In both cases the curves of calculated and observed pressures are of similar shape, the calculated values being, as before, larger than those observed. The close agreement noticeable in fig. 6 may reasonably be ascribed to the low frequency of oscillation (26 cycles per minute), and provides an interesting confirmation of the effects of frequency on viscosity and inertia losses, as mentioned in the preceding paragraph.

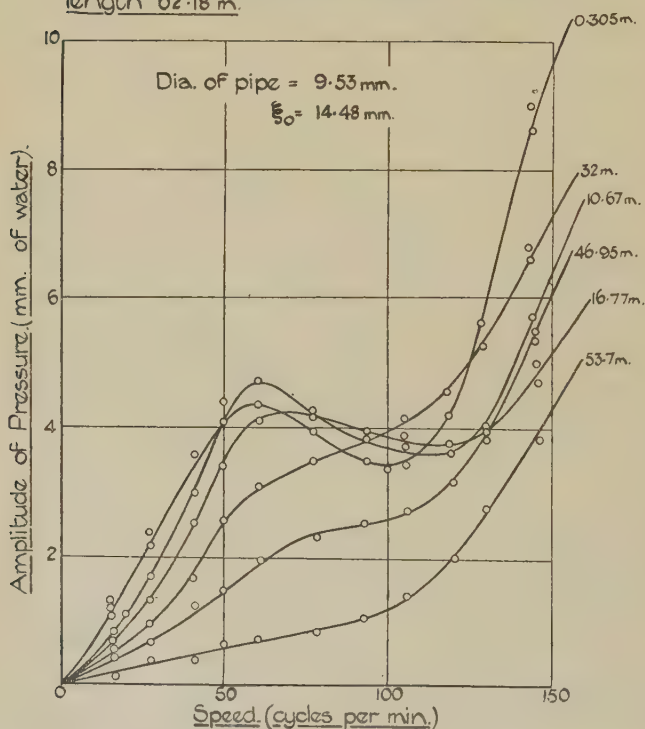
The curve of observed values plotted in fig. 7 is obtained from fig. 8 by cross-plotting, and provides a typical example of the variation of pressure along an open-ended pipe for frequencies not exceeding 60 per minute. In the example given, the pressure attains a maximum at or near the piston end; but it will be observed that at higher frequencies the maximum pressure occurs at other positions nearer the open end. There is a marked disparity between the calculated and observed values, which clearly demonstrates the need for a revised theory in closer agreement with observed facts.

Fig. 8 shows the relationship between frequency and pressure, measured at various distances from the near end, in an open pipe 62.18 m. in length and 9.53 mm. in diameter. For points within 18 metres of the near end the curves show the same characteristic feature of pressure amplitude increasing with rapidity of fluctuation up to a maximum value in the neighbourhood of 60 cycles per minute; from thence to about 120 cycles the pressure decreases slightly, but at higher speeds it tends towards a second and higher maximum value, possibly in the neighbourhood of 180 cycles per minute. At points along the pipe beyond 18 metres from the piston the first crest in the curve is absent, but there is in all cases a rapid increase of pressure at about 150 cycles per minute. This indication of the presence of a second peak value probably represents the pressure conditions with fair accuracy, although the actual values of pressure, as already stated, are somewhat uncertain owing to the difficulties associated with the measurement of fluctuating pressure at high speeds. It is reasonable to suppose that

these peak values indicate resonance between the applied motion and the natural vibrations in the pipe; the one at 60 cycles appears to correspond to the fundamental, and the second at 180 to the first overtone. Theoretically, in a frictionless fluid, the pressure should reach infinity simultaneously at all points along the pipe, and the

Fig. 8.

Pressure Amplitude measured at Various Distances along an open-ended Pipe of length 62.18 m.



extent to which this rule is violated in practice is evidence of the influence of viscosity in modifying the motion of air in the pipe. The unexpected result that the pressure at 180 cycles is greater than that at 60 cycles has not been satisfactorily explained.

From a consideration of the frequencies and pipe-lengths at which resonance occurs it is possible to form a rough estimate of the velocity of wave propagation. Calculations

of this velocity have been made from the observed results given in Table III., in fig. 5, and in the following Table, which refers to observations of displacement made by means of a soap-film at the end of 9.53 mm. bore pipes of various lengths, the frequency being maintained constant at 150 cycles per minute :—

TABLE IV.

Length of Pipe (m.).	Amplitude of Displacement, (mm.).
3.05	13.0
15.24	21.2
24.38	29.2 (max.)
30.48	21.2
45.72	10.8
60.96	8.4

The values for the velocity of wave propagation obtained from the conditions of resonance observed during measurements of *displacement* receive an interesting confirmation from a similar value obtained by a consideration of the resonance conditions indicated by the *pressure* curves of fig. 8. The calculations are approximate only, and the simple equation

$$\xi = A \sin (nt - qx) + A \sin \{nt - q(2l - x)\},$$

from which viscosity terms are omitted, has been deemed sufficiently accurate for the present comparison. In the following Table references are given to the sources from which the wave velocities are determined; the velocities refer to pipes of 9.53 mm. bore in all cases:—

TABLE V.

Velocity of Wave Propagation. (m. per sec.)	Frequency at Resonance. (cycles per minute.)	Resonance Observation.
228	150	From displacement: Table III.
234	115	„ „ : Table IV.
229	75	„ „ : fig. 5.
249	60	From pressure: fig. 8.

In the determination of the last value in this table, a mean figure of 60 cycles per minute has been taken for the frequency at which resonance occurs.

From a few measurements of displacement at the end
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of a pipe of 4.75 mm. bore, a velocity of propagation amounting to 59 m. per second is obtained. It may be concluded, therefore, that in general the velocity of wave propagation diminishes rapidly with reduction of pipe diameter; but within the limits of experimental accuracy no appreciable effect of frequency on that velocity can be detected.

In conclusion it may be stated that the present paper is not intended to provide a theory of the transmission of air-waves through pipes. It aims at no more than a comparison of existing theories with the results of experiment. The investigations completed up to the present serve to illustrate a few of the more serious sources of error met with in full-scale work, and indicate the necessity for the introduction into such work of more refined apparatus than has hitherto been employed; for whilst the general problem of viscous flow in pipes may not be insoluble, it remains probable that the difficulty of determining and expressing with mathematical exactness the complex terminal conditions likely to be encountered in the practical measurement of fluctuating pressures, will prove to be greater than that of making use of forms of apparatus in which long transmission pipes are not constituent parts. The essential features of such apparatus appear to be a gauge of very small internal volume and very light moving parts, situated at the point where the fluctuating pressure exists, and an electrical method of transmitting the pressure reading to a central station.

Finally, the writers desire to acknowledge their indebtedness to Mr. R. V. Southwell for his helpful criticism and advice and to Mr. A. H. Bell for his assistance during the early part of the experimental investigation.

LIX. *On the Combined Vibration of a Bar and String, and the "Wolf-Note" of a Stringed Instrument.* By W. B. MORTON, M.A., and FLORENCE M. CHAMBERS, M.Sc., Queen's University, Belfast*.

1. Introduction.

THE small motion of the ends of a vibrating string plays an important part in the action of a stringed instrument, inasmuch as it is the link by which the energy is

* Communicated by the Authors.

transferred to the body, and so to the air. In general, the effect of this yielding of the supports on the pitch is only slight, but it is well known that in instruments of the violin family the interaction of string and body is such that it makes impossible the steady production of one particular note, the so-called "wolf-note."

The late Lord Rayleigh* treated the matter in a general way by supposing that the string was fastened at each end to a mass which was acted upon by a spring, idealizing in this way the inertia and elasticity of the body of an instrument on which the string is stretched. The system made up of the mass and spring has a natural frequency of its own. The effect of the yielding of the ends is to raise or lower the pitch of a note according as it is higher or lower than this critical pitch—in other words, the pitch of the string moves away from that of the supporting system. A further discussion on similar lines is included in Prof. Raman's important monograph on the motion of strings†.

By way of supplementing and illustrating this general method of treatment, it appears of some interest to examine a definite special case in which the motion can be worked out in detail. The case of a string stretched along a uniform bar suggests itself as a rough model or simplification of a stringed instrument. On theoretical grounds also it is interesting to study the coupling together of two elastic bodies which, taken separately, obey such entirely different laws of vibration. The investigation, undertaken with this general point of view, led to a result which seemed to have a possible bearing on the phenomenon of the wolf-note.

2. *Theory.*

A string and bar are joined at their ends by short transverse connecting pieces of negligible mass. Let origins be taken at the centre of each, and let the transverse displacements of string and bar be denoted by y, η respectively. For simple harmonic oscillations of frequency $p/2\pi$ the form of the string is given by

$$y = A \cos qx + B \sin qx,$$

where the periodic factor is omitted, and

$$q^2 = p^2 m / l T,$$

m, l, T being mass, length, and tension of the string.

* 'Text-book of Sound,' vol. i. p. 135.

† "Indian Association for Cultivation of Science," Bulletin 15, p. 119.

The tension of the string will produce a permanent thrust in the bar of the same constant magnitude to a first approximation. We must, in the first instance, take account of this thrust in considering the vibrations of the bar, though it will appear later that its effect on the frequencies is small. Accordingly, the differential equation satisfied by the curve of the bar is

$$\frac{d^4\eta}{dx^4} + 2s^2 \frac{d^2\eta}{dx^2} = r^4\eta,$$

where

$$2s^2 = T/EI,$$

$$r^4 = p^2 M/lEI,$$

M, E, I being mass, Young's modulus, and moment of inertia of cross-section.

The general solution is

$$\eta = \alpha \cos r_1 x + \beta \sin r_1 x + \gamma \cosh r_2 x + \delta \sinh r_2 x,$$

where

$$r_1^2 = (r^4 + s^4)^{\frac{1}{2}} + s^2,$$

$$r_2^2 = (r^4 + s^4)^{\frac{1}{2}} - s^2.$$

The conditions to be satisfied at the ends $x = \pm \frac{1}{2}l$ are

- (1) Equality of displacements, $\eta = y$;
- (2) Vanishing of bending moment, $d^2\eta/dx^2 = 0$;
- (3) Equality of shear in the bar and the component of the tension transverse to the bar,

$$EI d^3\eta/dx^3 = T(dy/dx - d\eta/dx).$$

We write

$$\frac{1}{2}ql = \theta, \quad \frac{1}{2}rl = \phi,$$

$$\frac{1}{2}r_1 l = \phi_1, \quad \frac{1}{2}r_2 l = \phi_2.$$

The terminal conditions give

- (1) $\alpha \cos \phi_1 + \gamma \cosh \phi_2 = A \cos \theta,$
 $\beta \sin \phi_1 + \delta \sinh \phi_2 = B \sin \theta ;$
- (2) $-r_1^2 \alpha \cos \phi_1 + r_2^2 \gamma \cosh \phi_2 = 0,$
 $-r_1^2 \beta \sin \phi_1 + r_2^2 \delta \sinh \phi_2 = 0 ;$

- (3) After some reduction,

$$r_2 \alpha \sin \phi_1 + r_1 \gamma \sinh \phi_2 = -TqA \sin \theta / EI r^2,$$

$$r_2 \beta \cos \phi_1 - r_1 \delta \cosh \phi_2 = -TqB \cos \theta / EI r^2.$$

The constants A, α, γ which belong to the even modes of vibration are separated from B, β, δ of the odd modes.

At this stage it is necessary to examine the way in which the unknown quantity p occurs in the magnitudes which have been introduced, and to separate it out from the constants of the problem. It enters in the first power in θ , and so we may take θ as representing the frequency of a note given by the system. In fact, the wave-length in the string is $\pi l/\theta$, so that the pitch of the note is determined when θ is known along with the physical constants of the string. For the fundamental of the string, vibrating with fixed ends, $\theta = \frac{1}{2}\pi$.

The quantity ϕ involves $p^{\frac{1}{2}}$, so θ/ϕ^2 is a constant, viz., $2(mEI/MTl^2)^{\frac{1}{2}}$; we denote it by c . In connexion with the third terminal condition, the quantity $Tq/EI\tau^3$ comes into the analysis. This contains $p^{-\frac{1}{2}}$; we put it $= k/2\phi$, where $k = (mTl^2/MEI)^{\frac{1}{2}}$.

The two constants c, k admit of simple expression in terms of two others which have immediate physical meaning. In the investigation of the motion of such a coupled system one would expect to find as determining factors the ratio of the masses of the two members and the ratio of their elasticities or stiffnesses. For the latter we may take, in the present case, the ratio which the tension of the string bears to the force EI/l^2 determined by the bar, being $1/\pi^2$ of the minimum force capable of buckling the bar. Accordingly we put

$$\begin{aligned}\mu &= m/M \text{ (mass ratio),} \\ \epsilon &= Tl^2/EI \text{ (stiffness ratio).}\end{aligned}$$

Then

$$\begin{aligned}c &= 2(\mu/\epsilon)^{\frac{1}{2}}, \\ k &= (\mu\epsilon)^{\frac{1}{2}}.\end{aligned}$$

An immediate acoustical significance can be attached to the quantity c . Multiplied by a certain number it gives the interval-ratio between a definite proper pitch of the string and a definite proper pitch of the bar. Here, and afterwards, when string and bar-pitches are mentioned, it is supposed that the string has fixed ends and the bar has free ends. If we take the fundamental pitches in both cases we have, for the string,

$$\begin{aligned}\theta &= \frac{1}{2}\pi, \\ p &= \pi(T/ml)^{\frac{1}{2}};\end{aligned}$$

for the bar,

$$\begin{aligned}\phi &= 3\pi/4 \text{ approximately,} \\ p &= 9\pi^2(EI)^{\frac{1}{2}}/4(Ml^3)^{\frac{1}{2}}.\end{aligned}$$

So (bar-frequency)/(string-frequency)

$$= 9\pi(mEI)^{\frac{1}{2}}/4(MTl^2)^{\frac{1}{2}},$$

$$= 9\pi c/8.$$

Under ordinary circumstances k is small, while c may have any magnitude.

Returning now to the determining equations (1), (2), (3), we eliminate the arbitrary constants and obtain "period-equations" for the even and odd vibrations in the rather complicated forms—

Even :

$$\phi(\rho_2^3 \tan \phi_1 + \rho_1^3 \tanh \phi_2) = -k \tan \theta (1 + \sigma^4)^{\frac{1}{2}}.$$

Odd :

$$\phi(\rho_2^3 \cot \phi_1 - \rho_1^3 \coth \phi_2) = -k \cot \theta (1 + \sigma^4)^{\frac{1}{2}}.$$

In these we have written

$$\rho_1 = r_1/r,$$

$$\rho_2 = r_2/r,$$

$$\sigma = s/r;$$

so that

$$\rho_1^2 = (1 + \sigma^4)^{\frac{1}{2}} + \sigma^2,$$

$$\rho_2^2 = (1 + \sigma^4)^{\frac{1}{2}} - \sigma^2.$$

We have $\rho_1 \rho_2 = 1$, but both symbols are retained for the sake of symmetry.

An interesting way of checking the accuracy of the analysis in this and similar questions is to verify that the angular momentum of the system, as it passes through the centre of the swing, is zero. For even modes this is ensured by the symmetry on the two sides of the centre; but for an odd mode it implies the vanishing of the angular momentum for half the bar and string taken together. The expression of this reduces to the equation

$$\int_0^{\frac{1}{2}l} (M\eta + my)x dx = 0;$$

putting

$$y = B \sin qx,$$

$$\eta = \beta \sin r_1 x + \delta \sinh r_2 x,$$

we get

$$M\{\beta(\sin \phi_1 - \phi_1 \cos \phi_1)/r_1^2 - \delta(\sinh \phi_2 - \phi_2 \cosh \phi_2)/r_2^2\} \\ + mB(\sin \theta - \theta \cos \theta)/q^2 = 0.$$

When the values of β , δ given by the first and second

terminal conditions are put in, this reduces to the period-equation.

The equations as they stand are quite intractable, since p , which is sought, occurs in ρ_1, ρ_2, σ as well as in $\theta, \phi, \phi_1, \phi_2$. A great simplification is effected if σ^2 can be neglected in comparison with unity, and under ordinary conditions this is the case. On putting in the values it will be found that

$$\sigma^2 = k/4\theta ;$$

k is a small fraction, while θ , in the most interesting cases, is near a multiple of $\frac{1}{2}\pi$, corresponding to a pitch given by the string. If σ^2 is neglected, ρ_1, ρ_2 become unity and $\phi_1 = \phi_2 = \phi$. We thus obtain—

Even modes:

$$\phi(\tan \phi + \tanh \phi) = -k \tan \theta ;$$

Odd modes:

$$\phi(\cot \phi - \coth \phi) = -k \cot \theta ,$$

with

$$\theta = c\phi^2.$$

The two constants c, k (or μ, ϵ) determine the distribution of the proper pitches of the combined system, *i.e.* the ratios of their frequencies. Having obtained a pair of values of $\theta\phi$ satisfying these equations, we can express the forms of string and bar by the equations—

Even:

$$y = A \cos \frac{2x\theta}{l} \Big/ \cos \theta ,$$

$$\eta = \frac{1}{2}A \left\{ \cos \frac{2x\phi}{l} \Big/ \cos \phi + \cosh \frac{2x\phi}{l} \Big/ \cosh \phi \right\} .$$

Odd:

$$y = B \sin \frac{2x\theta}{l} \Big/ \sin \theta ,$$

$$\eta = \frac{1}{2}B \left\{ \sin \frac{2x\phi}{l} \Big/ \sin \phi + \sinh \frac{2x\phi}{l} \Big/ \sinh \phi \right\} .$$

When k vanishes the equations break up into those which give the vibrations of a string with fixed ends and a free-free bar separately, *viz.*,

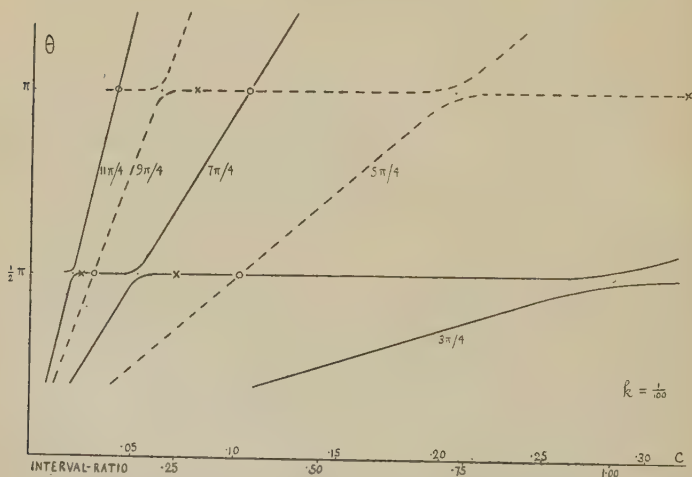
$$\text{Even:} \quad \tan \phi + \tanh \phi = 0, \quad \tan \theta = \infty .$$

$$\text{Odd:} \quad \cot \phi - \coth \phi = 0, \quad \cot \theta = \infty .$$

In the above analysis the usual practice has been followed of neglecting the effect of the rotatory inertia of the bar.

Before proceeding to the discussion of the simplified period-equation, it is worth while to compare the small influence which the neglected term has upon the frequency with that exerted by the thrust in the bar. To take the rotation of the sections into account the term $\frac{Mp^2}{AlE} \frac{\partial^2 \eta}{\partial x^2}$ has to be added to the differential equation already discussed. Here A is the area of the cross-section. The effect is merely to change the meaning of the coefficient $2s^2$, and to add to σ^2 a term which reduces to $(2\kappa^2\phi^2/l^2)$, where κ is the radius of gyration of the section. The ratio of this to the former σ^2 is $(4\kappa^2\theta^2/l^2\mu)$. Here the small quantity $\mu=m/M$ in the denominator counteracts the smallness of κ^2/l^2 , so the two small effects may be comparable in magnitude.

Fig. 1.

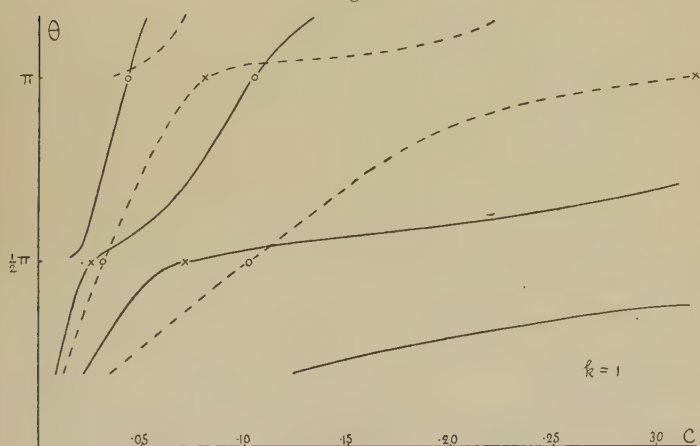


To examine the solutions of the period-equation for the combined system as simplified, we assume a definite value for the constant k . Then for each value of ϕ we can calculate θ , and thence $c=\theta/\phi^2$. The results are shown by plotting θ against c . On the diagram are drawn a series of lines radiating from the origin, $\theta/c=\phi^2$, for values of ϕ in odd multiples of $\pi/4$. The values $3\pi/4$, $7\pi/4$, etc., correspond very nearly to the even modes of vibration of the bar by itself, and $5\pi/4$, $9\pi/4$, etc., to the odd modes.

The diagram (fig. 1) has been drawn for $k=.01$. The even and odd modes are indicated by full and broken lines respectively. When a vertical is drawn through the proper

value of c , it meets the various branches at heights proportional to the frequencies of the notes given by the compound system. It will be seen that in general these consist of string-notes slightly modified by the yielding of the ends of the bar and bar-notes modified by the presence of the string. With this value of k the divergences are inappreciable, except near the gaps, where the bar-lines run off into string-lines. For clearer illustration of the course of the curves the exaggerated fig. 2 has been drawn for $k=1$. The graduations marked below the axis give the interval-ratio $9\pi c/8$.

Fig. 2.



The curves fall to the origin in a succession of cascades. The falls have the approximate direction of the radiating lines which represent the undisturbed frequencies of the bar, and run from a gap in one string-level to a gap in the next level of the same kind (even or odd). The intermediate level of the other kind is crossed at points marked with a circle. After the fall the curve runs inwards close to the horizontal line, crossing it at a point marked with a cross and dropping in another fall from the next gap.

The curves are not carried down to the origin, to indicate that the simplified equations lose their significance for small values of θ when σ^2 ceases to be negligible. For this reason a branch, belonging to the odd equation, along which θ and ϕ are small, is omitted. It would indicate a mode of vibration, having a single node at the centre, which is mechanically impossible. There is no physical interest to justify an

examination of the way in which the origin is approached by the exact curves. As θ approaches zero the quantity ρ_1 becomes infinite, so the terms $\tan \phi_1$ and $\cot \phi_1$ introduce essential singularities.

There are three kinds of special points to be considered, viz., those in the centre of the gaps and the points marked with a circle and with a cross. The first and second are alike cases of resonance, when there is coincidence between a bar-note and a string-note, but the two are distinguished by quite different effects:—

(1) At the gaps the coincident notes correspond to bar and string vibrations which are of the same kind—both even or both odd. Such a pitch cannot be elicited from the combined system. In place of it there are two displaced pitches, producing “resonance with beats.” When the bar and string frequencies coincide exactly the number of beats is a minimum; mistuning in either direction makes them come faster.

To examine this analytically we take the even equation,

$$\tan \theta = -\phi (\tan \phi + \tanh \phi)/k.$$

When k is small the right-hand side is in general large, and θ lies near an odd multiple of $\pi/2$. If $\delta\theta$ is the displacement of the proper pitch of the string,

$$\delta\theta = k/\phi (\tan \phi + \tanh \phi),$$

with $\phi = (\theta/c)^{\frac{1}{2}}$, the approximate value being put for θ . This approximation fails if c is such that the value $\theta = (2n+1)\frac{\pi}{2}$ makes $(\tan \phi + \tanh \phi)$ a small quantity; in other words, when this value of θ nearly corresponds to an even mode of the bar also. We know that even in this case, for small k , the deviation from the undisturbed string-frequency is small, so we may write

$$\begin{aligned} \phi(\tan \phi + \tanh \phi) &= \phi(\sec^2 \phi + \operatorname{sech}^2 \phi)\delta\phi \\ &= (\sec^2 \phi + \operatorname{sech}^2 \phi)\delta\theta/2c, \end{aligned}$$

which gives

$$\begin{aligned} \delta\theta &= 2ck/(\sec^2 \phi + \operatorname{sech}^2 \phi)\delta\theta, \\ \delta\theta &= \pm \{2ck/(\sec^2 \phi + \operatorname{sech}^2 \phi)\}^{\frac{1}{2}}. \end{aligned}$$

Here ϕ has one of the values lying close to $3\pi/4$, $7\pi/4$, etc., so as an approximation we may neglect $\operatorname{sech} \phi$ and put $\sec^2 \phi = 2$, giving

$$\delta\theta = \pm (ck)^{\frac{1}{2}} = \pm (2m/M)^{\frac{1}{2}} \text{ approximately.}$$

The same result is arrived at for the odd modes.

When the fundamentals of bar and string coincide,

$$\theta = \pi/2. \quad \phi = 3\pi/4, \quad c = \theta/\phi^2 = 8/9\pi.$$

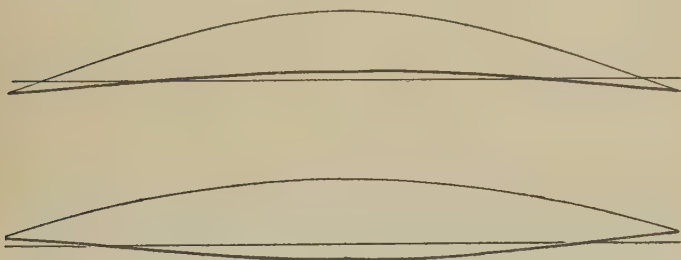
For $k = .01$ this gives

$$\begin{aligned} \delta\theta &= \pm .05 \text{ roughly,} \\ &= 3^\circ \text{ say.} \end{aligned}$$

This agrees with measurement made on the graph.

The forms of bar and string are shown on an exaggerated scale on fig. 3, with $\delta\theta = \pm 10^\circ$, $\theta = 90^\circ$.

Fig. 3.



(2) When an even frequency of the string coincides with an odd frequency of the bar, or *vice versa*, the note is given unaltered by the combination; for the period-equations are satisfied, for any value of k , if we have at the same time $\tan \theta = 0$ and $\tan \theta + \tanh \phi = 0$ or $\cot \theta = 0$ and $\cot \theta - \coth \phi = 0$.

The corresponding points are marked with a circle. They are the intersections of the level $\theta = \frac{\pi}{2}$ with the lines

$$\phi = 5\pi/4 \quad \text{at} \quad c = 8/25\pi = .102$$

$$\text{and} \quad \phi = 9\pi/4 \quad \text{at} \quad c = 8/81\pi = .031,$$

and of $\theta = \pi$ with

$$\phi = 3\pi/4 \quad \text{at} \quad c = 8/9\pi = .283$$

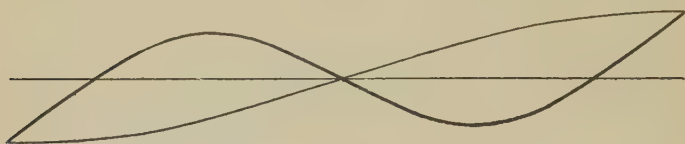
$$\text{and} \quad \phi = 7\pi/4 \quad \text{at} \quad c = 8/49\pi = .052.$$

Here, and elsewhere, the approximate values are taken for ϕ .

In this motion the bar vibrates as if it were alone; the string has loops at its ends instead of nodes, so that an even

mode is changed into an odd one having the same wave-length in the string (fig. 4). The string exerts no influence on the vibration of the bar because the tensions at the ends have no transverse component. It is to be noted that, for the same values of k and c , there is another mode of vibration, with a very slightly higher pitch, in which the string vibrates with its ends almost motionless. The raising of the pitch implies shortening of the wave-length, so that the nodes fall a little inside the ends of the string. On the graph for

Fig. 4.



$k = .01$ the point which represents this node is indistinguishable from that marked with a circle; the separation can be seen on fig. 2. Since the energy of the motion is conveyed to the air by the bar, this second note will be scarcely audible in comparison with the other. Under ordinary conditions the two notes will, in any case, be too close to give beats, and also a very small displacement, in the direction of increasing c , brings us to the intersection of the bar and string curves, with complete fusion of the two frequencies and disappearance of beats. Therefore this kind of resonance may be called "resonance without beats," to distinguish it from that indicated by the gaps in the curves.

(3) In the motion just discussed, a natural pitch of the string when vibrating with fixed ends is yielded by the combined system. There is another case in which this occurs, when the ends of the string actually are fixed points. The period-equations are satisfied when both sides become infinite, which happens if, for a particular value of c , we have at the same time

$$\text{(Even mode)} \quad \tan \theta = \infty, \quad \tan \phi = \infty,$$

$$\text{(Odd mode)} \quad \cot \theta = \infty, \quad \cot \phi = \infty.$$

Confining attention to the fundamental of the string,

$\theta = \frac{1}{2}\pi$, this pitch is given unaltered if, along with this,

$$\phi = \pi/2, \quad 3\pi/2, \quad 5\pi/2, \text{ etc.,}$$

i. e. if $c = 2/\pi, \quad 2/9\pi, \quad 2/25\pi, \text{ etc.,}$
 $= \cdot 637, \quad \cdot 071, \quad \cdot 025.$

The corresponding points on the diagram are marked with a cross.

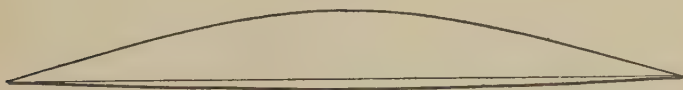
The form of the string is now $y = A \cos \pi x/l$, so the ends are nodes. Equation (2) shows that the constant γ vanishes, the hyperbolic term disappears from the equation of the bar, and it also vibrates in a sine-curve. The relation between the amplitudes of the string and bar-curves is given by the third terminal conditions

$$\begin{aligned} \alpha/A &= -k \sin \theta/2\phi \sin \phi \\ &= -k/\pi, \quad k/3\pi, \quad -k/5\pi, \\ &= -\mu, \quad 3\mu, \quad -5\mu, \dots \end{aligned}$$

since $ck = 2\mu$.

The tangents to the string and bar at the motionless ends always slope on opposite sides of the horizontal (fig. 5).

Fig. 5.



Similarly, the first overtone of the string is given unaltered with motionless ends when

$$\begin{aligned} \theta &= \pi, \\ \phi &= \pi, \quad 2\pi, \quad 3\pi, \dots \\ \text{and } c &= 1/\pi, \quad 1/4\pi, \quad 1/9\pi \dots \\ &= \cdot 319, \quad \cdot 080, \quad \cdot 036. \end{aligned}$$

3. Experiments.

In order to test the theory some experiments were made, the "bar" being a piece of light metal tubing such as is used for a kind of gong. It was a little over a centimetre in diameter and 54 cm. long. On this a steel pianoforte wire of

29 S.W.G. was mounted in the following manner. At one end of the tube a coned brass sleeve was inserted transversely, and into this fitted a conical brass peg with a cross-piece. At the other end a slit was made along the diameter of the tube parallel to the axis of the peg, and a small bridge was soldered to the tube above this. A knot was made on the wire, which was then slipped into the slit, drawn tightly over the bridge, and passed through a hole in the peg. By means of the peg the string could be tuned to any desired pitch and held by friction of peg against sleeve. The range of tension was such that either the first or second overtone of the string could be brought into coincidence with the first overtone of the bar. The system was suspended horizontally, with the string underneath, by cords attached to the outer nodes of the bar in this (odd) mode of vibration.

The system was kept in forced oscillation by the action of periodic force applied by a small electromagnet, through which passed the alternating current from a triode valve. The frequency of this was altered by means of a variable inductance in the circuit.

The natural frequencies of the system are indicated by maximum response.

The various pitches were expressed in terms of the corresponding lengths of a standard sonometer wire. The alternating current from the valve passes through this wire, which runs between the poles of a strong electromagnet, fed with a steady current. The reaction between the alternating valve-current and the field gave rise to a periodic force on the sonometer wire. The length of wire giving maximum resonance is inversely proportional to the frequency of the alternations.

After a frequency of the combined system had been determined in this manner, for a definite tension of the wire, the bar was clamped and the measurement repeated so as to get the corresponding string-pitch with fixed ends. The length of sonometer wire corresponding to the bar-pitch used was found by the method of beats.

The following effects were observed:—

(1) When the string and bar-pitches are not close together a large visible motion of the string was obtained at the proper frequency of the applied force, but only a very faint sound was heard. The motion of the ends of the string is now very small, and its proper pitch very slightly displaced.

(2) When the pitch of the second (even) overtone of the string is approaching that of the first (odd) overtone of the bar the amplitude of the string motion decreases, but the

note becomes louder. When the pitches coincide there is no visible movement of the string while a loud sound is produced by the bar. The string has a node at the centre, loops at the ends and at the points of trisection. This is the case of "resonance without beats."

(3) When the first overtone of the string (odd) is near the first overtone of the bar (odd) there are two different frequencies of the applied force which produce loud sounds. As the string-pitch approaches the bar-pitch from below, the upper of the two resonances rises from the bar-pitch. When the coincidence is exact the two resonances are at equal distances above and below the common pitch of string and bar. As the string-pitch rises higher the lower resonance approaches the bar-pitch from below. The observed amplitude of the string-motion is large, being maximum when coincidence is exact. This case of "resonance with beats" was examined quantitatively in the manner explained above, the lengths of sonometer wire being determined for the resonance-pitches and the string-pitch for a series of tensions of the wire. The first and second lengths are then plotted against the third.

For a theoretical graph to compare with these measurements we cannot use the representation of fig. 1, in which k is constant and the independent variable is c . This has to be modified so that $\mu = \frac{1}{2}kc$ is constant. For the coincidence of the pitches in question we have

$$\theta = \pi, \quad \phi = 5\pi/4, \quad c = 16/25\pi = \cdot 2037.$$

The experiments therefore cover ranges of $c\phi$ extending on the two sides of these values.

The equation to be satisfied is

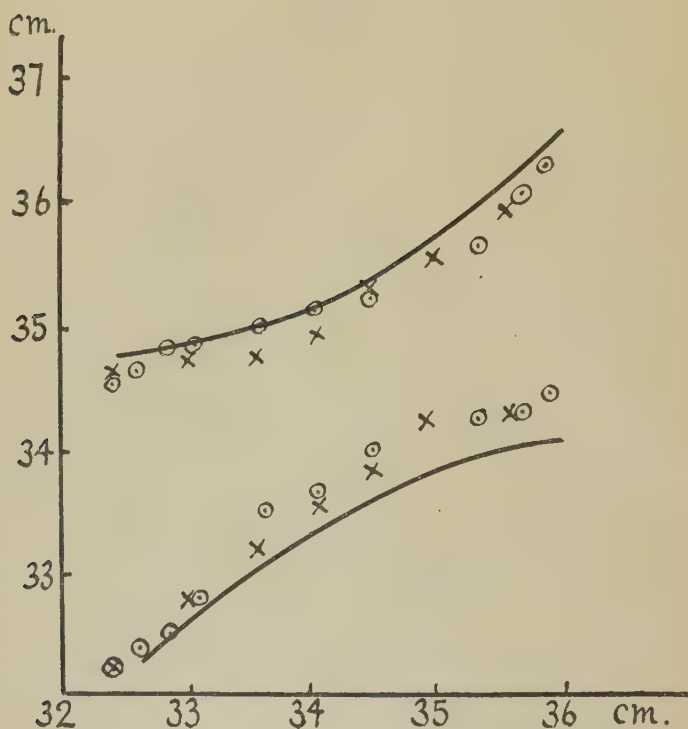
$$\phi(\coth \phi - \cot \phi) = k \cot c\phi^2.$$

For a series of values of c running from $\cdot 190$ to $\cdot 230$ the corresponding values of $k = 2\mu/c$ were calculated. For the bar and string used in the experiments $\mu = m/M = \cdot 00317$. Then the set of curves $y = k \cot cx^2$ was drawn along with the curve $y = x(\coth x - \cot x)$ for the range of x between $\cdot 210$ and $\cdot 240$. The intersections give the values of ϕ for each c . The resonance frequencies are proportional to ϕ^2 and the string-frequency is inversely as c . The length of the sonometer wire corresponding to the bar-note was $34\cdot 4$ cm. Accordingly the magnitudes plotted in the experimental graph are got by calculating

$$34\cdot 4 \times c/\cdot 2037 \quad \text{and} \quad 34\cdot 4 \times (225)^2/\phi^2.$$

The result is shown in fig. 6. The readings obtained in two series of experiments are shown marked with a circle and a cross respectively.

Fig. 6.



4. Wolf-Note.

It remains to consider the possible bearing of the above theory on the curious phenomenon of the "wolf-note." It is generally agreed that the difficulty in producing this note is due to its coinciding with a proper pitch of the body of the instrument, a kind of resonance not to be confused with the resonance of the enclosed mass of air, as investigated by Helmholtz. Assuming this, we have first to inquire which of the two kinds of resonance is more likely to be concerned. The question is not easy to decide *à priori*, and it seems possible that resonance of either kind might produce the effect. Consider first that without beats. Here there is

a possibility of a sudden change in the mode of vibration of the string at the critical frequency, passing from the normal manner in which the motion is large in the centre and small at the ends to the type of fig. 4, with the middle point of the string at rest and the ends moving largely. One would expect such a transition to upset the ordinary technique of bowing and to prevent the bow from biting properly. On the other hand, under the forcing action of the bow the formation of the central node may in actual fact be prevented, and so the normal mode of vibration be retained.

The other kind of resonance is more in accordance with the fluctuating nature of the motion, as shown in the photographic records taken first by White and afterwards by Raman *. The displacement-time curves for points on the string and belly are like those given by two beating vibrations. White regarded the fluctuations as beats between a natural frequency and that impressed on the instrument by the bow. Raman pointed out that such beats of forced vibrations would occur only at the beginning of the action of the applied force, before the establishment of the permanent *régime*. He found the explanation of the fluctuations in his theory of the action of the bow. According to this theory, a bow which presses on the string with a given force and moves with a given velocity can maintain the fundamental vibration only so long as the rate at which energy is withdrawn from the string at its ends remains below a certain limit. When this is exceeded the mode of vibration alters into a type in which the octave predominates. When the wolf-tone is sounded on the string the resonance builds up an exceptionally large motion of the body, accompanied by a rapid withdrawal of energy from the string. Then the mode of vibration changes, resonance ceases, the rate of loss of energy falls below the limit, the normal action of the bow is restored, and the process is repeated in regular cycles.

The plate which accompanies Prof. Raman's paper shows simultaneous traces of the motion of a point on the string and a point on the belly of a violoncello taken by the method used by Prof. Barton and his pupils. Both traces show the periodic changes, each cycle containing about sixteen vibrations. In agreement with the theory, the maxima of the body-movement follow those of the string by about a quarter-period of the cycle, and at the minima the octave harmonic is clearly evident. The string-vibration at the

* White, Proc. Camb. Phil. Soc. xviii. p. 85 (1915); Raman, Phil. Mag. xxxii. p. 391 (1916).

maxima has the familiar zigzag form. The curve at the minima resembles that which is obtained when the fundamental component is omitted from the harmonic analysis of this form as given by Helmholtz*. The scale of the photograph is too small to permit of an exact verification of this. The vibrations of the body, reproduced on a much larger scale, are rather irregular in appearance, and seem to consist of the fundamental, mainly or altogether, except at the minima where the octave shows up.

One is tempted to connect the beat-like course of the vibrations, as revealed by these photographs, with the two close frequencies shown to exist for the free vibrations of the bar-string system in "resonance with beats." It might be supposed that the fundamental in the Fourier series for the rectilinear form of vibration was replaced by two slightly displaced frequencies, each having half the amplitude and beating together. Beginning in phase with each other, they would build up the zigzag form. When the phase-difference amounted to a half-period they would cancel and give the intermediate form with predominant octave. This appeared plausible, but when the wave-forms were plotted by calculation on this basis, for comparison with the observed trace, it was found that the rectilinear forms returned only after *two* periods of the beats. The reason is that at the first return of maximum amplitude of the combined vibration the phase is reversed in relation to the remaining terms of the harmonic series. The displacement

$$\begin{aligned} & \sin 2\pi n_1 t + \sin 2\pi n_2 t \\ &= 2 \cos \pi(n_1 - n_2)t \cdot \sin \pi(n_1 + n_2)t \end{aligned}$$

has its amplitude

$$= 2 \quad \text{for } t=0,$$

$$\text{but} \quad = -2 \quad \text{for } t=1/(n_1 - n_2).$$

If in the graph of the resultant displacement we measure from a crest at one maximum to a crest at the next we shall find the distance to differ by a half wave-length from an integral number of waves. Thus the distance between the recurrences of the rectilinear vibration-forms for the string should be twice that between the maxima for the fundamental vibrations of the body, whereas these distances are equal on the photograph.

* 'Sensations of Tone' (Ellis), Appendix VI. p. 384.

The phenomenon of "resonance with beats" cannot therefore be invoked as an explanation of the observed cyclical phenomena at the wolf-pitch, and we are left with Prof. Raman's theory, which relies solely on considerations of energy-transfer, and makes no reference to modes of vibration of the combined system of string and body. It is possible that the ignoring of frictional forces in our theory has deprived it of any applicability to the actual case of a stringed instrument, but it is difficult to think that there is no connexion between a note which does not exist as a free vibration, in the one instance, and a note which is difficult to produce as a forced vibration in the other.

There is one observation recorded in Raman's paper which seems to indicate the existence of the two different kinds of resonance. The effect of a mute attached to the bridge was examined, and was found to be a lowering of the pitch of the wolf-note. A load of 40.4 gms. was found to depress the frequency from 176 to 137, and also to cause "two new but comparatively feeble resonance-points to appear at 100 and 184 respectively, without any attendant cyclical phenomena."

Raman has also published * a photograph of the motion of string and bridge when the 'cello is played pizzicato at the wolf-note pitch. This is a case of a free vibration, but the damping is so great that any cyclical character which the motion might possess could not readily be detected on the graph. The amplitude of the string-motion is greatest just after the release, while that of the bridge rises to a maximum after five or six vibrations; but this lag is conditioned, in part at any rate, by the fact that we are dealing with the beginning of the motion when the "initial conditions" still influence the form.

One or two fresh points in connexion with the wolf-note phenomenon were suggested by some observations made at our request by Mr. L. McCann, B.Sc., who is a skilled violin-player. On the only violin on which he could find a wolf-note this lay high up on the E string, at the pitch B, a twelfth above the note of the open string. When the tension of the string was relaxed the wolf was still found at the same pitch, *i. e.* with a shortened string. When the open pitch of the string was brought down to C, the exceptional character of the note B began to disappear, and was quite gone at B flat.

The constancy of the wolf-note pitch agrees with the idea

* 'Nature,' vol. ci. p. 264 (1918)

that it corresponds to a proper pitch of the body of the violin, but there are two points difficult to explain. The first arises from the high frequency of the note, about 1980. This cannot be the fundamental pitch of the body. If it is an overtone, why is the wolf-effect not found on the lower proper pitches?

We made an attempt to determine roughly the proper pitches of a violin, regarded as a bar of variable mass-distribution, using the method given by Lord Rayleigh for such a case ('Sound,' vol. i. pp. 114 & 291). We were encouraged to try this by the successful application of the method by T. C. Tobin to calculate the proper periods of large ships *. We used the tabulated values of the functions involved which are given in his paper. The use of the same mathematical machinery to deal with a liner or a violin is a rather striking instance of the unimportance of the linear scale. The values found were as follows:—

	First approximation.	Second approximation.
Fundamental	464	455
First overtone.....	1289	1236
Second overtone.....	2526	2454

This leaves it doubtful whether the wolf-note found by Mr. McCann was the first or second overtone. It is to be remembered that our measurements were made on a different violin.

The other point is the disappearance of the wolf-note with the lowered tension of the string. This may perhaps be explained on Raman's theory if we suppose the decreased force between string and body implies a smaller transference of energy at the ends. On the other hand, it involves also a shortening of the string and a consequent decrease of the ratio m/M , causing the gaps on our graph to close up.

In the hope of obtaining fresh light on some of the points raised in this section, we intend to try the experimental method described in the second part of this paper to find the proper periods of a violin which has a marked wolf-note.

* Inst. of Naval Architects, Paper No. 6 (1922).

LX. *The Electrical Conductivity of some Dilute Liquid Amalgams.* By E. J. WILLIAMS, M.Sc., Late University Research Student at University College, Swansea*.

OBSERVATIONS on the electrical conductivity of amalgams have been made by various workers, notably Larsen †, Weber ‡, and Matthiesen and Vogt §. The problem has been considered theoretically by Skaupy ||, who has made use of the experimental results obtained by the above-mentioned observers. The variation of the relative conductivity with temperature, and the nature of the departure of the variation of the relative conductivity with concentration from a linear law, are quantities of considerable theoretical interest, and in order to obtain reliable values of these it is necessary to have accurate and comprehensive data. The observations which have been referred to include only a few made at temperatures higher than 100° C., whilst the results for the lower temperatures due to different observers are not always in agreement. The object of the present work was to provide accurate data covering a greater range of temperature, and to extend observations to amalgams of metals not previously investigated. This paper ¶ mainly deals with the experimental results obtained in the case of cadmium amalgams, which had been previously investigated by several observers **, and also in the case of magnesium and indium amalgams, which had received no attention previously ††.

For the sake of comparison with the amalgams and also for testing the accuracy of the experimental method, the electrical conductivity of pure mercury was measured over the range 0° C. to 300° C.

* Communicated by Prof. E. J. Evans, University College of Swansea.

† *Ann. Physik*, (4) i. p. 127 (1900).

‡ *Wied. Ann.* xxiii. p. 471 (1884).

§ *Phil. Mag.* xxiii. p. 161 (1862).

|| *Deutsch. Phys. Gesell. Verh.* xviii. p. 252; *Phys. Zeits.* p. 597 (1920).

¶ The observations are being continued by another worker.

** Larsen, *Ann. der Physik*, (4) i. p. 127 (1900); Weber, *Wied. Ann.* xxiii. p. 471 (1884); Calvo, *Ion*, ii. p. 408 (1910); Borneman & Rauschenplatt, *Metallurgie*, ix. pp. 473 & 505 (1912); E. von Schweidler, *Sitzber. Akad. Wien*, civ. p. 278 (1895); A. Battelli, *Atti Accad. Lincei*, (4) iv. p. 206 (1887); R. S. Willows, *Phil. Mag.* [5] xlviii. p. 445 (1899); Vicentini & Cattaneo, *Atti Accad. Fisicocritici*, (4) lxxv. pp. 147, 227 (1893).

†† Willows (*Phil. Mag.* [5] xlviii. (1899)) made observations on the conductivity of an amalgam containing 1 per cent. of magnesium, but as the amalgam was in the solid state it does not concern us.

Experimental Arrangement.

The resistance was measured by means of a Callendar and Griffiths Bridge, which when used in conjunction with a delicate galvanometer enabled the resistance to be measured with an accuracy of $\cdot 0001$ ohm, this corresponding to a tenth of a millimetre of the bridge-wire. Nothing would be gained by determining the resistance with greater accuracy, since $\cdot 0001$ ohm corresponded to the change of resistance produced by the smallest change of temperature measurable in these experiments. The various resistances of the bridge were calibrated in terms of the largest resistance by the usual method. A knowledge of the absolute values of the resistances of the bridge was not necessary for determining the relative change of the resistance of an amalgam due to change of temperature or composition. It was, however, necessary that the various resistances of the bridge should be consistent amongst themselves, which was ensured by the calibration.

The resistance to be measured was connected to the bridge by flexible leads about two yards long, and compensating leads, connected to terminals provided for them on the bridge, were used to avoid effects produced by changes of resistance of the leads during the periods of making measurements.

The amalgam was contained in a capillary tube which opened out into two vertical limbs as shown in fig. 1 *a*. Into these limbs fitted the leads as shown in fig. 1 *b*.

The copper wire *c* was connected to the bridge, and also to the amalgam in the capillary by means of the mercury *m* and the platinum wire *p*. The copper wire was kept in a fixed position by means of a capillary *b* in order that the resistance of the leads be maintained constant during measurements. In making a determination of resistance, the resistance with the leads in the same amalgam cup was first measured and then with the leads in the limbs of the capillary tube. The difference between the two resistances was the difference between the resistances of two columns of amalgam at the same temperature *t*; the resistance of the leads cancelling out. The two columns referred to are the column between the platinum terminals when in the same amalgam cup, and that between them when in the limbs of the capillary. The former is of course almost negligible in comparison with the latter, but this need not be assumed. In all the measurements these two columns were the same, so that the difference between their resistances, or what will

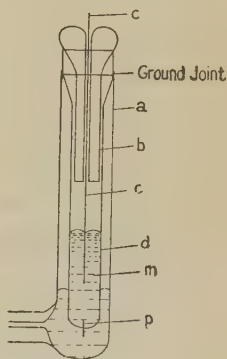
be henceforth called the resistance of the amalgam, was proportional to the resistivity at that temperature*.

For measurement of resistance at 0°C . a bath containing melting ice was used, and for measurement at room temperature a water bath. At all higher temperatures the amalgam columns were immersed in a boiling liquid; the agitation of the liquid caused by boiling ensuring a uniform temperature. The following is a list of the liquids used with their respective approximate boiling-points in $^{\circ}\text{C}$. :—water (100), alcohol (129), aniline (184), diethyl aniline (221), eugenol (256), glycerine (288), diphenylamine (300). Some of the liquids did not boil at a constant temperature with continued heating, the temperature increasing gradually as they

Fig. 1. *a*.



Fig. 1. *b*.



were boiled. In those cases, the observations were not made until the rate of variation of temperature became sufficiently small to warrant an accurate determination of resistance and temperature. The time taken by the capillary tube and amalgam to assume the temperature of the bath was inappreciable and caused no trouble. In all cases, however, a series of readings of temperatures and resistances was made to ensure a reliable result.

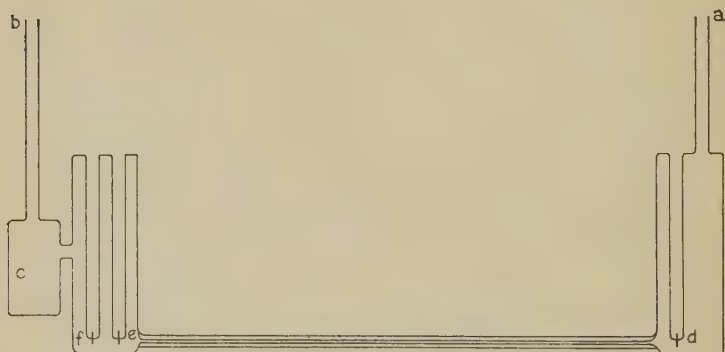
Two thermometers were used to determine the temperature; the one a platinum thermometer and the other a mercury thermometer. A set of mercury thermometers graduated in tenths of a degree and certified by the National Physical Laboratory was used. The difference between the temperatures recorded by the two thermometers respectively

* This statement applies to the relation between the resistivity and the resistance of the amalgam when the latter is corrected for the expansion of the capillary tube.

did not in general exceed $0^{\circ}2\text{ C.}$ and when the difference was greater it was probably due to disuniformity in the temperature of the bath.

One of the difficulties met with was the formation of bubbles in the capillary tube at the higher temperatures. There was greater tendency for this to happen in tubes of small diameter, and at the higher temperatures tubes of narrow bore (diameter $< 0.7\text{ mm.}$) were not used. This formation of bubbles could be avoided to a large extent by heating the amalgam to a temperature not far from its boiling-point before and after adding it to the capillary tube, and in the latter case removing any bubbles that formed. If after an experiment no bubbles were present in the tube it could be assumed that none had formed at the high

Fig. 2.



temperature, and therefore that the result obtained was free from any uncertainty arising from this effect. The values of the resistivity at high temperatures obtained by some observers are high compared with those obtained in the present experiments, and probably the discrepancy arises from the formation of bubbles in the tubes used by these observers.

Magnesium amalgams readily oxidized when exposed to the air, and in order to prevent this oxidation, magnesium amalgams were prepared and added to the capillary tube in a vacuum, the entire process being carried out in a sealed glass tube shown in fig. 2. The mercury was added at *a*, and the magnesium at *b*, the magnesium falling into the side vessel *c* and kept separated from the mercury. The tube was then evacuated and the open ends *a* and *b* sealed. The mercury was then poured into vessel *c* on to the magnesium,

and the amalgam prepared. The amalgam was then poured back into the capillary tube and the resistance measurements made. The resistance of the leads could not be eliminated exactly as before because the platinum lead *d* could not be detached and put in the same cup with *e*. An extra lead *f* was therefore provided near the lead *e*, the ratio of the effective resistance of *f* to that of *d* and *e* being determined by preliminary observations at room temperature.

Variation of the Resistance of Pure Mercury with Temperature within the range 0°–300° C.

Two series of observations were made, one with a capillary tube (A) of diameter 0.5 mm. giving a resistance of the mercury of about 1.7 ohms at room temperature, the other with a tube (B) of diameter .7 mm. and giving a resistance of the mercury column of .8 ohm. The results are given in Table I.

α_t = average temp. coeff. from 0° to t° , i. e., $\frac{r - r_0}{r_0 t}$;

α_c = average temp. coeff. from 0° to t° corrected for expansion of the glass tube *;

ρ_t and σ_t are the values of the resistivity and conductivity respectively at t° , the conductivity at 0° C. being, by definition of unit resistance, 10630.

TABLE I.

Temperature t .	$\alpha_t \times 10^4$.			$\alpha \times 10^4$.	$\rho_t \times 10^9$.	$\sigma_t \times 10$.
	With Tube A.	With Tube B.	Weighted Mean.			
0° C.					94074	106300
16.8	8.99	8.97	8.983	9.066	95507	104705
100	9.772	9.760	9.768	9.861	103351	96758
129	10.064	10.077	10.068	10.169	106415	93972
184	10.622	10.614	10.619	10.734	112635	88766
221	10.999	11.000	10.999	11.121	117194	85329
256	11.395	11.390	11.393	11.521	121820	82086
288		11.716	11.716	11.853	126188	79245
297		11.824	11.824	11.964	127509	78423

* The values of the linear expansion coefficient were determined for the glass capillary tube used, for different ranges of temperature. It increased with the temperature, the observed value for the range 0°–100° being 8.6×10^{-6} , and for the range 0°–180°, 9.6×10^{-6} .

The estimated probable error in α (excluding the room temperature value) is on the average about $\cdot 15$ per cent. The difference between the values of α_t obtained with tubes A and B respectively is nowhere greater than this. Various formulæ have been proposed to represent the variation of the resistivity of mercury with temperature. The values of the resistivity at different temperatures obtained in the present experiments can be represented by a quadratic formula to within $0\cdot 5$ per cent. This deviation is, however, greater than the experimental error, the estimated probable value of which is about $0\cdot 02$ per cent. By introducing a cubic term into the formula the resistivity can be represented with a maximum deviation of only $0\cdot 25$ per cent. and an average deviation of $0\cdot 15$ per cent. The formula is :

$$\rho_t = \rho_0 \{1 + 0\cdot 8879 t + 0\cdot 975 t^2 + 0\cdot 20 t^3\} \quad . \quad (1)$$

A very accurate determination of the resistivity at 100° relative to that at 0° has been made by Jager and Steinwehr *. The value of the resistivity at 100° given by the above formula agrees to within $0\cdot 1$ per cent. with their value. The only previous data that have been found for temperatures above 100° are due to Vicentini and Omodei †, and Benoit ‡. The values of the temperature coefficient obtained by the former for the ranges 0° – 100° and 0° – 300° are about $\cdot 7$ per cent. greater than those obtained here, whilst for ranges from 0° to intermediate temperatures the values given are about 2 per cent. greater. The values of the temperature coefficient obtained by Benoit are on the whole about 2 per cent. less.

CONDUCTIVITY OF AMALGAMS.

The results of the observations on the amalgams of cadmium, indium, and magnesium are given in Table II. A brief discussion of the results, which will also serve to explain the table, will now be given.

Cadmium Amalgams.

Two specimens of cadmium were used, one obtained from Harrington, London, and the other from Kahlbaum, Germany. The resistances of amalgams of equal concentrations prepared from each of these specimens were found to be the same to within experimental error.

* *Ann. d. Physik*, (4) xliii. p. 1165 (1914).

† *Atti Accad. Torino*, xxv. p. 30 (1889).

‡ *Comptes Rendus*, lxxvi. p. 341 (1873).

The values of the conductivity changes at room temperature for concentrations ranging from .009 per cent. to 4 per cent. are given in the first part of Table II. p is the weight of cadmium per unit weight of amalgam, δ is the relative increase of conductivity, that is,

$$\frac{\text{conductivity of amalgam} - \text{conductivity of mercury at the same temp.}}{\text{conductivity of mercury}}$$

and a is the estimated rate of variation of the relative increase of conductivity with concentration at infinite dilution.

The values of b in column 6 measure the departure of the variation of the conductivity with concentration from a linear law. The constancy of b (the variations are within experimental error for amalgams containing less than 2 per cent. of cadmium) shows that the variation of the conductivity of dilute amalgams with p obeys a quadratic law, the conductivity, c , of an amalgam of concentration p being given by

$$c = c_0 \{ 1 + 7.80 p - 20 p^2 \}.$$

Skaupy, as the result of an analysis of Larsen's results, concludes that the variation of the conductivity of dilute cadmium amalgams deviates considerably from a quadratic

law. Except for very weak amalgams the values of m , $= \frac{\delta}{p}$,

obtained in the present experiments and those obtained by Larsen agree to within about 0.5 per cent. The weakest amalgam investigated by Larsen contained .0163 per cent. of cadmium, and the value of m obtained for this was 9.8, which marked a sudden increase over the values obtained for the higher concentrations. There is no evidence whatever in the present results of the existence of such an increase in m . Regarding as real this sudden increase Skaupy estimated $\lim_{p \rightarrow 0} m$ as 10.8, and as a result could not represent

the conductivity by a quadratic formula.

The results obtained at different temperatures show that the relative increase of conductivity, δ , increases uniformly with the temperature, the percentage increase being independent of the concentration of the amalgam to within experimental error. The actual magnitude of the increase with temperature is comparatively small, the increase in δ due to an increase of temperature from 0° to 300° C. being only 20 per cent. of its value at 0° C. Bornemann and Rauschenplatt* have made observations on the conductivity of dilute

* *Loc. cit.*

cadmium amalgams at high temperatures, and they give results for two amalgams whose concentrations expressed in atoms per cent. are 0.99 and 3.02 respectively. The ratio of the values of δ at 100° , 200° , and 300° calculated from these results is 1.00 : 1.07 : 1.00. The ratio according to the results obtained in the present experiments is 1.00 : 1.06 : 1.14.

Indium Amalgams.

Indium was found to pass readily into solution in mercury. Two different specimens of the metal were used, and were found to give the same results to within experimental error. Owing to the limited supply of the metal, amalgams containing more than 3 per cent. of indium were not investigated, and only a limited number of amalgams of lower concentrations could be used.

It is seen from the table that the variation of m with concentration is small, and the value of b is consequently uncertain. The relative increase of conductivity increases with the temperature, and as in the case of cadmium amalgams, the percentage increase is independent of concentration. The increase is greater than for cadmium amalgams, the percentage increase due to an increase of temperature from 0° to 100° being 8 for indium amalgams as compared with 4 for cadmium amalgams.

Magnesium Amalgams.

Magnesium in the form of ribbon was used. Although the metal dissolved in mercury at ordinary temperatures, the rate of dissolution was greatly increased by warming the mercury. If prepared in the presence of air the magnesium was not retained in the amalgam; the resistance of the filtered liquid being the same as that of pure mercury. This was due to the rapid and complete oxidation of the magnesium contained in the amalgam, an effect which had been previously noticed by many observers. This oxidation was prevented by employing a method which has already been described in the account of the experimental arrangement.

It was found that on cooling an amalgam containing 0.2654 per cent. of magnesium, the conductivity increased suddenly at about 4°C and then continued to increase irregularly. The variations were attributed to the separating out of solid from solution, and an examination of the amalgam showed the presence of solid floating on the surface. It was concluded, therefore, that an amalgam containing 0.2654 per cent. of magnesium is saturated at 4°C .

In consequence of this comparatively small "magnesium content" of mercury, only three amalgams were investigated. The change of conductivity was, however, so great that accurate measurements could be made.

Relative increase of Conductivity and Atomic Concentration of the Metal.

In the last column of Table II. are given the values of the ratio of the relative increase of conductivity at infinite dilution to the concentrations expressed in atoms of the metal per atom of mercury. Skaupy* has found that this quantity, A , is approximately the same for amalgams of different metals. This conclusion means that atom for atom the effects of different metals on the conductivity of mercury are the same. The results which have been obtained in this investigation for indium and magnesium amalgams are new, and were therefore not included amongst those considered by Skaupy. It is therefore interesting to find that the values of A for cadmium and indium respectively are very nearly the same; the values at room temperature being in the ratio 1 : 0.95. A for magnesium is somewhat high in comparison, being 41 per cent. greater than A for cadmium. It is worth noticing, however, that weight for weight there is not the slightest trace of equivalence between the effects of cadmium and magnesium upon the conductivity of mercury; the respective values being in the ratio 1 : 6.5.

The variation with temperature is small and is in the same direction for the three metals, and consequently the relative values of A do not change much with temperature. The ratio $A_{\text{Cd}} : A_{\text{In}} : A_{\text{Mg}}$ at 184° C. is 1 : 1.02 : 1.41 as compared with 1 : 0.95 : 1.41 at 14° C.

SUMMARY OF RESULTS.

The values obtained for the resistivity of mercury at various temperatures within the range 0°–300° C. are represented by the formula

$$\rho_t = \rho_0 \{ 1 + 0.38879t + 0.6975t^2 + 0.920t^3 \}$$

to within the probable experimental error, the estimated value of which is .02 per cent. The resistivity at 100° C. according to this formula differs only by .01 per cent. from a determination made by Jager and Steinwehr (1914).

The results obtained for cadmium amalgams show that the

* *Loc. cit.*

TABLE II.

Nature of Amalgam.	Temp. °C.	Conc., $p, \times 10^2$.	$\delta \times 10^2$.	$m = \frac{\delta}{p}$.	$\frac{\alpha - m}{p} = b$.	$\frac{\alpha - \text{It. m.}}{p=0}$.	A.
Cadmium Amalgams.	14°	·0087	·06 ₉	8		7·80	4·37
		·0437	·33 ₈	8			
		·0654	·51 ₃	7·8			
		·1129	·87 ₈	7·7 ₃	2×10		
		·2742	2·13 ₀	7·7 ₆	$1\frac{1}{2} \times 10$		
		·4379	3·36 ₉	7·6 ₉	$2\frac{1}{2} \times 10$		
		·7152	5·45 ₉	7·6 ₃	24		
		·9825	7·45 ₇	7·59	21		
		·9913	7·54	7·60	20		
		1·4741	11·05	7·50	20		
		1·9608	14·50	7·40	20		
		2·9566	21·49	7·27	18		
		3·8423	27·36	7·12	$17\frac{1}{2}$		
	100°	·505	4·05	8·0	$2\frac{1}{2} \times 10$	8·12	4·58
		·728	5·77	7·9 ₃	$2\frac{1}{2} \times 10$		
		·9913	7·84	7·92	20		
		1·9608	15·09	7·70	21		
		2·9566	22·47	7·59	18		
		3·8423	28·51	7·43	18		
	0° 184° 302°	·9913	7·49	7·56		7·76	4·35
		·9913	8·27	8·35		8·55	4·80
		·9913	9·00	9·00		9·29	5·22
Indium Amalgams	14°	·107	·75	7·0		7·20	4·14
		·498	3·51	7·0 ₄			
		1·062	7·56	7·12			
		1·845	13·19	7·15			
		1·933	13·74	7·12			
		3·043	21·30	7·00			
	100°	·498	3·80	7·60		7·75	4·45
		1·062	8·13	7·65			
		1·933	14·84	7·67			
		3·043	22·96	7·55			
	0° 184°	1·933	13·60	7·05		7·13	4·10
		1·933	16·30	8·44		8·52	4·90
Magnesium Amalgams.	14°	·0524	2·65	50·7		50·7	6·18
		·1181	5·93	50·2			
		·2654	13·18	49·7			
	100°	·1181	6·23	52·8		53·3	6·51
		·2654	13·96	52·7			
	0° 30·8 184°	·1181	5·88	49·8		50·3	6·14
		·2654	13·08	49·3		50·3	6·14
		·2654	15·08	54·6		55·6	6·78

conductivity of dilute amalgams (containing < 2 per cent. Cd) can be represented to within experimental error by a quadratic formula, the relative conductivity at 14° C. of an amalgam containing p parts of Cd in 1 part of amalgam being given by $1 + 7.80p - 20p^2$. The departure of the variation of the conductivity of indium amalgams with concentration from a linear relationship is small, whilst in the case of magnesium amalgams it could not be accurately tested as amalgams containing about $\frac{1}{4}$ per cent. of magnesium are saturated at room temperature.

The estimated values of $a, = \lim_{p \rightarrow 0} \frac{c - c_0}{c_0 \cdot p}$, where c is the conductivity of an amalgam of concentration p at 14° C. and c_0 is the conductivity of pure mercury at the same temperature, for indium and magnesium amalgams respectively are 7.20 and 50.7, as compared with 7.80 for cadmium amalgams.

The effects of these metals, atom for atom, upon the conductivity of pure mercury are sensibly the same, a result in agreement with an empirical relation obtained by Skaupy as the result of consideration of amalgams of other metals (including cadmium, however). The values of $A, = \lim_{p' \rightarrow 0} \frac{c - c_0}{c_0 \cdot p'}$, where p' is the atomic concentration, for Cd, In, and Mg respectively, are 4.37, 4.14, and 6.18.

Results are given showing the effect of temperature upon the conductivity of Cd amalgams over the range 0° – 300° C. and of In and Mg amalgams over the range 0° – 184° C. The change of relative increase of conductivity with temperature

is small, the values of $\frac{a_{(100^{\circ})}}{a_{(0^{\circ})}}$ for Cd, In, and Mg amalgams being 1.041, 1.077, and 1.060 respectively, the relative increase being independent of the concentration to within experimental error. As a result of the smallness of the temperature effect, the extent of the agreement with Skaupy's rule is very little affected by considering values of conductivity at different temperatures. The ratio of the values of A_{Cd}, A_{In}, A_{Mg} , which relate to values of conductivity at 184° C., is 1 : 1.02 : 1.41 as compared with the value 1 : 0.95 : 1.41 of the ratio of the values relating to room temperature conductivities.

In conclusion I wish to express my warm thanks to Professor E. J. Evans for his most valuable assistance during the course of the work.

LXI. *The Electric Charge carried by Thorium X and Thorium Emanation Recoil Atoms in Gases.* By G. H. BRIGGS, B.Sc.,
Lecturer in Physics in the University of Sydney *.

THE charge carried by recoil atoms, resulting from the decay of the radio-active emanations when the latter are mixed with a gas, has been the subject of numerous investigations. Wellish† was the first to show definitely that the recoil atoms of radium active deposit at the end of their recoil path in air, hydrogen, and carbon dioxide are either positively charged or neutral. In two papers‡ the writer has described experiments by which values were found for the percentage of the recoil atoms positively charged at the end of their recoil paths in various gases, for Ra A recoiling from Ra Em and Ra B from Ra A. It was shown also that the behaviour of the active deposit of Th Em in an electric field is explained, if it is assumed that in any gas the percentage of Th A atoms positively charged at the end of their recoil path is the same as for Ra A, and that a similar relation holds for Th B and Ra B. This similarity in the behaviour of isotopic atoms also gave a satisfactory explanation of Lucian's§ results for the active deposit of Actinium emanation. It is probable that the recoil atom during its recoil path through the gas captures and loses electrons in much the same manner as positive rays and α particles do, and that the final charged state at the end of the recoil path is a matter of chance, depending on the nature of the collisions near the end of the path and not on the initial velocity of the recoil atom. Identical results would not be found for isotopic recoil atoms if the charge at the end of the recoil path were dependent on the initial velocity. The present paper describes experiments in which Th X and Th Em were examined from the same point of view.

PART I.—*Thorium X.*

Two very simple methods of preparing sources which give appreciable amounts of Th X by recoil were tried and proved satisfactory:—(a) A platinum disk, diameter 2 cm., was platinized just sufficiently to produce a slight tarnish, and a small quantity of mesothorium bromide dissolved in water

* Communicated by Sir E. Rutherford, F.R.S.

† Phil. Mag. xxviii. p. 417 (1914).

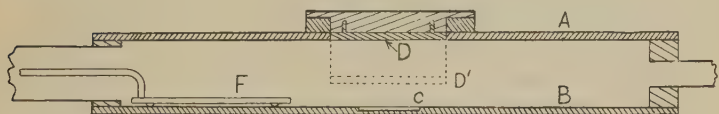
‡ Phil. Mag. xli. p. 357 (1921); P. Roy. Soc. N.S.W. lvii. 249 (1923).

§ Phil. Mag. xxviii. p. 761 (1914).

was spread over the surface and allowed to dry. (b) Radiothorium was separated in the usual way from mesothorium, the precipitate carrying down the radiothorium being allowed to settle on a similar platinum disk. The gamma-ray activity of the former source was equivalent to that of 0.15 mg. radium and the latter to that of 0.10 mg. Both of these sources gave Th X, and also Th A and Th B by recoil. These products were readily collected on a negatively charged electrode, an exposure of one minute giving sufficient Th X to be easily measured with a Dolazalek electrometer having a sensitivity of a few hundred millimetres per volt. It will be shown later, however, that the efficiency of recoil was only about 3 per cent.

The exposure apparatus consisted of a box, shown in longitudinal section in fig. 1, made of two brass plates A and B separated by ebonite. Its internal dimensions were

Fig. 1.



$16 \times 4.3 \times 2$ cm. The source C was placed in a recess so that it was flush with the bottom of the box, and the recoil atoms were collected on a circular brass plate D, which in some experiments was flush with A, and in others, when in the position D', was only 7 mm. from B. The time of activation of the plate D was controlled by moving with an electromagnet a slider F which covered the source. To carry off Th Em escaping from the latter, a current of the gas under test was maintained through the box at a mean velocity of about three centimetres per second. The gases were dried with phosphorus pentoxide and filtered. In order to obtain saturation of the recoil atoms more readily in the presence of the intense ionization from the source, the working pressure was always maintained in the neighbourhood of 10 cms. Voltages up to 1200 were used; the time of exposure was generally 15 or 20 minutes. The activated disks were covered after removal with thin aluminium foil to prevent the escape of Th Em produced by the decay of the Thorium X collected, and their α -ray activities were measured at various times during the next 6 or 10 days. Often a series of exposures were made, using the gas and air alternately. The order of making the exposures did not influence

the result in any definite manner, although there was sometimes difficulty in obtaining values consistent to within less than 2 per cent.

The percentage of Th X positively charged in air was found by making exposures in which the source and the disk to be activated were separated by only 0.4 mm. and the pressure was reduced to 0.005 mm. Under these conditions all the atoms recoiling from the source should strike the disk. The ratio of the amount of Th X collected in this way to the amount collected in air in an equal time at a pressure of 10 cm., the distance between the source and the disk D being 7 mm. and the voltage 400, was found in successive experiments to be 100.0, 100.2, and 99.4 per cent. It is concluded therefore, that in air all the Th X recoil atoms are positively charged at the end of their recoil paths.

The experimental results obtained by comparing the amount of Th X collected in various gases with that collected in air are given in the second column of Table I. The third column gives the electric force.

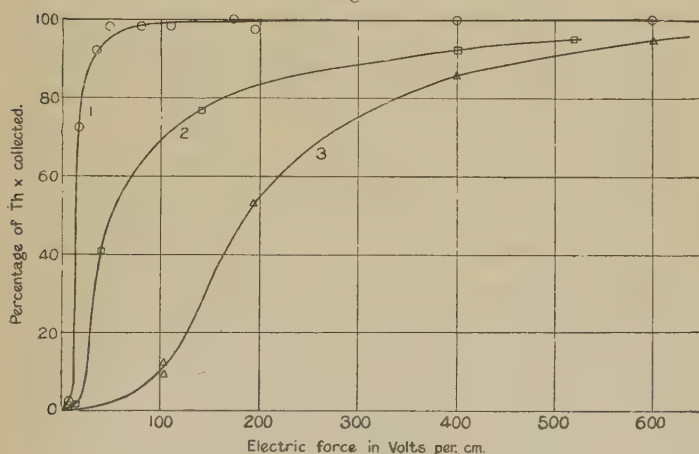
TABLE I.

Gas.	Ratio of the amount of Th X collected in gas to the amount collected in air $\times 100$.	Electric force in volts per cm.
Helium	99.9	600
Oxygen	101	530
Hydrogen	100.2	600
Nitrogen	100.0	530
Carbon dioxide.....	99.7	600
Nitrous oxide	99	600
Acetylene	101	400
Ammonia	94.6	530
Ethyl ether	94.7	600
Methyl acetate	94	800
Ethyl acetate	94	800
Acetone	90	800
Methylal	87	570
Hexane	90	500

In these experiments the ionization from the source is very intense, saturation of the ions being obtained in air at

atmospheric pressure only with an electric force of 250 volts per cm. In fig. 2 are curves showing how the amount of Th X collected on the upper plate varied with the electric force in the case of air and ammonia at 12 cm. pressure and in ethyl ether at 10 cm. pressure. It is seen that saturation of the Th X atoms is much more difficult to obtain in ammonia than in air and more difficult still in ether. From the upward trend of the curves for ether and ammonia it appears that at sufficiently high voltages they would coincide with that for air. This is probably true for all the other

Fig. 2.



Saturation curves for Thorium X recoil atoms in :

1. Air.
2. Ammonia.
3. Ethyl ether.

gases or vapours which give experimental results below 100 per cent. The experiments had to be discontinued before this point could be more thoroughly investigated, but it seems fairly safe to conclude that not only in the first seven gases of Table I., where the values differ from 100 per cent. by less than the experimental error, but also in ammonia and all the vapours investigated the Th X atoms are all positively charged at the end of the recoil path. This is in marked contrast to the behaviour of Th A and Ra A or Th B and Ra B, as can be seen from Table II., which summarizes the results of the present experiments and those given in the two previous papers by the author.

TABLE II.

Percentage of recoil atoms positively charged
at end of recoil path.

	Th X.	Th Em.	Ra A and Th A.	Ra B and Th B.
Helium	100		93·7	>96·4
Oxygen	100	Zero	88 *	95 *
Hydrogen	100	Zero	82·4†	93†
Air.....	100	Zero	82·4	93
Nitrogen	100			
Carbon dioxide	100	Zero	71·8	83·2
Carbon monoxide.....	67 *	82 *
Argon	61·8	81·8
Nitrous oxide	100	...	61·8	79·8
Methane	15·9	78·1
Acetylene	100	...	2·2	74·9
Ammonia	100	...	Zero	69·4
Ethylene	"	61·8
Hydrogen sulphide	"	54·9
Ethyl ether	100	...	"	5·5
Methyl acetate	100	...	"	5·0
Ethyl acetate	100	...	"	3·5
Acetone	100	...	"	4·3
Methylal	100	...	"	3·7
Hexane	100	...	"	3·3

* Estimated from value for active deposit of Ra Em, Briggs (*loc. cit.*).

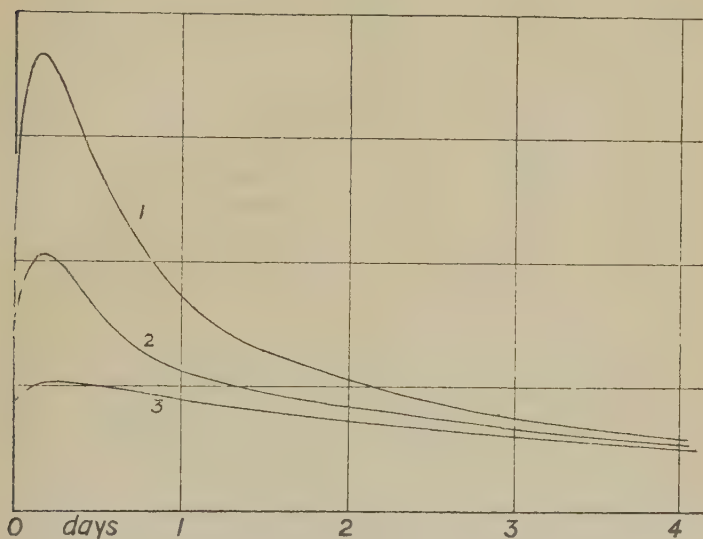
† " " " " Wellish (*loc. cit.*).

It may be asked whether these experiments in which the recoil occurs under very unfavourable conditions can yield trustworthy results. This question will be considered in the following sections, which give a more detailed account of the active deposit collected from these sources under various conditions.

Typical decay curves of the deposit collected in various gases are shown in fig. 3. In air the activity reaches a maximum in four hours, and after about six days decays with the period of Th X. The curve shows that in air the activated plate collects from the source a certain amount of Th A or Th B together with the Th X. The less marked maximum in the curve for ammonia shows that the total

amount of Th A + Th B collected is smaller than in air. In ether hardly any Th A or Th B is collected, and the activity decays almost as if it were due entirely to Th X. There is, however, just enough Th A or Th B present to mask the maximum which would be expected at the end of the first day if only Th X had been collected. Decay curves of this type were found with all the vapours examined.

Fig. 3.



Decay of α -ray activity of the deposit collected in :

1. Air.
2. Ammonia.
3. Ethyl ether.

To determine whether the Th A or Th B collected in air was received through recoil from the source or from the decay of free emanation which has escaped from the source, a sheet of metal was attached to the disk D on the down-stream side and in the same plane. The amount of Th A + Th B collected on this was measured at various distances along it and was found to be practically constant and, for an equal area, about 1 per cent. of the Th A + Th B collected on D. Hence the Th A and Th B collected on the activated disk is practically all due to recoil from the source. It may be noted that when the upper plate was positively charged no detectable activity was collected.

The efficiency of recoil from the source.

An approximate estimate of this quantity was made in the following manner. The total number of α rays emitted per second from the Radiothorium source was determined from the saturation-ionization current produced by it in air. It was assumed that α rays are emitted in equal numbers from the Radio Th, Th X, Th Em, Th A, and Th C present. This assumption neglects any escape of emanation from the source. Knowing the initial ionization current from the Th X collected in a given time, it was deduced that 1.25 per cent. of the total number of Th X atoms produced in the source escape by recoil, so that the actual efficiency of recoil of the Th X was 2.5 per cent. For the mesothorium source the efficiency was 3.5 per cent. It was also calculated from the decay curve that the mean efficiency of recoil of the Th A and Th B is about equal to that of the Th X. Owing to the fact that only a few per cent. of the recoil atoms escape from the plate, the equality which holds between the numbers of the various kinds of atoms transforming per second in the plate if none escaped is not appreciably disturbed as a result of recoil.

From decay curves, such as those shown in fig. 3 for the deposit when collected in air and in ammonia, it is possible to calculate the ratio " r " of the total number of Th A + Th B atoms collected in ammonia to the total number collected in air. Now, if the present method of experiment is justifiable, the ratio r should be able to be predicted from the previous results for Th A and Th B given in Table II., if in addition the ratio " s " of the number of Th B to the number of Th A atoms escaping from the source were known; s is then the ratio of the efficiencies of recoil of Th B and Th A. From Table II. it can be seen, for example, that for ammonia the ratio r should be

$$\frac{s \times 0 + 69.4}{s \times 82.4 + 93.0}.$$

It was impossible to measure s directly.

In Table III. are values of r for some of the gases used in the present experiments and the values calculated from the results previously published for the case when $s=1$ and for $s=1.8$, which is the value of s giving the best agreement. That it is possible to obtain this agreement for a series of gases, for which the percentage of Th A positively charged ranges from 82 to zero and of Th B from 93 to 70, is sufficient support for the results obtained in the

present experiments. The value 1·8 for s leads to the conclusion that the efficiencies of recoil of Th X, Th A, Th B in these experiments are as 1 : 0·78 : 1·40 ; the ranges of the α rays producing the recoil are as 1 : 1·16 : 1·31. These values for the efficiency of recoil neglect any escape of emanation. Some rough measurements indicated that about 10 per cent. of the emanation escaped from the source.

TABLE III.

Amount of Th A + Th B collected in gas $\times 100$.
 " " " in air

	Observed.		Calculated for	
		Mean.	$s=1\cdot8$.	$s=1$.
Carbon dioxide.....	87·5			
	85·3			
	93			
	90·5	89·1	88·7	88·4
Nitrous oxide	83·6			
	85·3			
	80·9	83·3	82·4	80·7
Acetylene	56·7			
	56·0			
	56·0	56·2	55·0	43·8
Ammonia	46·8			
	46·3			
	49·7			
	49·5			
	52·4			
	50·4			
	45·0	48·6	50·1	39·6

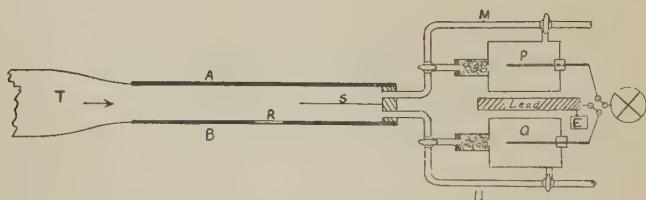
The decay curves for ether and the other vapours used show that a small amount of Th A or Th B is collected. From Table II. it is seen that the percentage of Th A positively charged in gases such as H_2S and NH_3 is zero, while the value for Th B is still quite large. It is most

probable therefore that the small amount collected in vapours in the present experiments is wholly due to a small percentage of the Th B recoil atoms being positively charged, while the Th A atoms are all neutral. This is the only conclusion which is consistent with the experiments in ether vapour made by Wellish (*loc. cit.*). He concluded that none of the active deposit of Ra Em was positively charged. However, as Ra B only played a minor part in his experiments, it is readily shown that if 5 per cent. of the Ra B atoms were positively charged in ether they would have produced an effect only of the same order as the experimental error. It is reasonable then to attribute the whole of the Th A + Th B activity collected in the vapours to Th B. In Table II. the percentages of Th B positively charged so obtained are given for the vapours of six liquids. They range from 3.3 per cent. to 5.5 per cent., but are probably not accurate to more than 1 in 5.

PART II.—*Thorium Emanation.*

Having found a method of obtaining Th X by recoil as described in Part I. the charged state at the end of the recoil path of Th Em recoiling from Th X was examined. The apparatus used is shown diagrammatically in fig. 4.

Fig. 4.



The right-hand end of the box AB described in Part I. was divided by a metal diaphragm S parallel to the plates A and B and midway between them. A stream of gas entering through the long tube T was thus divided, one half being led into an ionization chamber P and the other into a similar chamber Q. Either of the ionization chambers could be connected to a quadrant electrometer. When a disk activated with Th X by recoil was placed in the recess R and the plate A charged negatively, it was expected that the emanation atoms

recoiling from the disk would, if positively charged, travel across to A, give up their charge, and then be swept by the gas stream into the ionization chamber P. If uncharged the emanation atoms would be carried into the ionization chamber Q. To keep the field uniform the diaphragm was always maintained at the mean potential of the plates A and B, and to reduce the disturbing effect of eddies in the gas stream the tube T was about 80 cm. long and 4 cm. in diameter, the section being changed gradually to fit the rectangular end of the box. Some tests with smoke showed that no visible eddies were produced in air. The mean velocity of the gas through the box was generally about 5 to 10 cms. a second and the pressure atmospheric.

The procedure in an experiment was as follows:—A disk activated with Th X was placed in the recess, the electric field in the required direction was established between the plates, and a stream of gas was led through the box and out through the by-passes M and N. The two streams having been adjusted to equality a steady flow was maintained for some time, often more than an hour, and then the streams were allowed to pass through their respective ionization chambers. The ionization current in Q was always very large, and without any added capacity would have given an electrometer rate of 80 mm. a second. By observing the rate of decay on stopping the flow this current was plainly due to Th Em. With air, oxygen, and carbon dioxide no detectable current in P was found. The same result was obtained with various potential differences up to 400 volts with the top plate negative and also when it was positive.

In hydrogen it was found more difficult to get conclusive results. A small ionization current was obtained in P, which was unaltered by reversing the potential or by keeping both plates at the same potential, and was evidentially due to eddies in the gas or to diffusion of neutral emanation atoms from the neighbourhood of the disk into the upper half of the box. By replacing the diaphragm by one about half as long again with a circular aperture 2.5 cm. in diameter directly above the source the ionization current in P was found to be zero.

It appears then that Th Em recoil atoms in air, oxygen, carbon dioxide, and hydrogen are neutral at the end of their recoil paths. This is most probably true of all three radioactive emanations in any gases or vapours, the monatomic gases being perhaps exceptions.

Summary and Discussion.

A method of obtaining Thorium X by recoil has been described, and the following results for the charged state of Th X recoil atoms have been found.

In He, O₂, H₂, N₂, CO₂, N₂O, and C₂H₂ all the Th X recoil atoms are positively charged at the end of their recoil paths.

In six vapours examined and in NH₃ the percentage of Th X collected on a negatively charged electrode ranged from 87 to 94, and because of the difficulty in the experiments with these of obtaining saturation of the recoil atoms it is concluded that in these also all the Th X atoms are initially positively charged.

The charged state of the Th Em atom recoiling from Th X has been examined in air, Au, H₂, O₂, and CO₂, and it is found that in these gases all the recoiling atoms of Th Em are neutral.

The results of an earlier research on Ra A and Th A and Ra B and Th B led to the conclusion as is to be expected that in regard to the charge carried at the end of the recoil path isotopic atoms behave identically. Hence the results obtained apply to corresponding substances in the other radioactive series. Also the results for Ra B should give those for other atoms of atomic number 82 produced by an α -ray change, *i. e.* Ra D, Th D, and Ac D recoiling from Ra C', Th C', and Ac C' and Ra G from Polonium. The result for Th X should give also that for Meso-Th 1 recoiling from Thorium.

The factors which determine the probability of a recoil atom being positively charged or neutral at the end of its recoil path are complex. The recoil atom may be regarded during its passage through the gas as an atom at a high temperature which tends to lose electrons, the degree of ionization approaching an equilibrium state corresponding to the velocity at any instant. As its velocity becomes smaller the degree of ionization on the average becomes less and the recoil atom tends to complete its outer electron group. If we consider the results obtained for the four recoil atoms in any one of the gases investigated, except perhaps helium, there is strong evidence, although observations with Th Em were made only in four gases, that the number of positive recoil atoms is zero for Th Em and 100 per cent. for Th X, with intermediate values for Th A and Th B, the order in which the number increases being Th Em, Th A, Th B, Th X [in some cases Th A is zero as well as Th Em]. On Bohr's scheme the number of

electrons in the outer groups of these atoms are 8, 6, 4, and 2 respectively, and it is to be expected that a singly or doubly ionized Th X atom will not show a strong tendency to recapture electrons, whereas in the case of Th Em the tendency to revert to the neutral state with the complete group of eight will be marked. The intermediate percentages found for Ra B and Ra A are consistent with this point of view. The ionization potentials of the four atoms increase from about 5.1 for Th X to about 11 for Th Em, but there does not appear to be any reason for expecting the ionization potential to enter into the mechanism in a way that will completely account for the results, in particular that Th X atoms are all ionized, whereas Th Em atoms are all neutral at the end of the recoil path. It appears rather that the results are to be correlated with the chemical properties of the recoil atoms. It is of interest to note here that a similarity between the behaviour of the emanation atom and that of the α particle may be inferred from these experiments and those of Henderson* and Rutherford†, who found that the number of neutral α particles rapidly increases as the velocity becomes less. It is thus probable that the α particle comes to the end of its path as a neutral atom, which is precisely what the present experiments have shown to be the case for the emanation recoil atom.

In the case of either Ra A or Ra B one can examine the influence of the gas on the number of charged recoil atoms. Here the ionization potential of the gas does not seem very important, but, as was pointed out in an earlier paper, the ease of dissociation generally appears to be the dominating factor. Briefly, the hypothesis which was suggested was that at a collision at which the recoil atom dissociates a gas molecule, the recoil particle has a large chance of capturing electrons if positively charged, and at a non-dissociating collision, if its velocity has not fallen below a limiting value, it has a large chance of losing electrons. Thus in a very easily dissociated gas the recoil atom will continue to dissociate when its velocity is too small to ionize itself and the chance of it becoming neutral will be great. This still leaves argon in an anomalous position.

The mechanism is probably further complicated by chemical interaction between the recoil atom and the gas. The recoil atom may form temporary chemical association with some of the products of dissociation. The latter may have been ionized at the collision and when separation

* Proc. Roy. Soc. A, cii. p. 496 (1922).

† Phil. Mag. xlvii. p. 277 (1924).

takes place the positive charge may remain with the recoil atom. The chance of the recoil atom becoming charged in this fashion should vanish when the velocity of the recoil atom is so small that it has enough energy to dissociate molecules, but not sufficient to ionize as well.

The experiments described in this paper were made in the Physical Laboratory of the University of Sydney. The author is indebted to Professor Vonwiller for his interest during the progress of the work and to Sir E. Rutherford for his helpful criticism of the results.

Cambridge, April 1925.

LXII. *Vibrations of two Pendulums connected by a Spring.*
By V. N. SOLOVIEFF*.

[Plates XVIII-XX.]

A NUMBER of mechanical models of coupled electric vibrations have been described in the preceding volumes of this Magazine †. The double-cord pendulum of Prof. Barton, so thoroughly investigated in his three valuable papers, seems to be the best of them. It may be also preferred to the other models described in the previous works of Wien, Garbasso, Sellmeier, Oberbeck ‡, etc., as it represents the most ingenious combination as regards simplicity of theory, convenience of construction, and exactness of analogy. Nevertheless, this model scarcely satisfies the above-mentioned natural requests in fullest measure, because Prof. Barton, as well as his numerous predecessors and followers, is trying to imitate the difficult case of *magnetically-coupled circuits*. On the contrary, the case of *electric coupling*, being essentially similar to the practically more important case of inductive coupling, admits an easy mechanical treatment. So perhaps the present paper, in which the author describes a model constructed independently of the works of Prof. Barton (the Philosophical Magazine for 1915-22 was not received in Irkutsk until June 1924), will be of some interest.

The model consists of two high and massive supports,

* Communicated by the Author

† Prof. Barton and Miss Browning, *Phil. Mag.* xxxiv. p. 246 (1917), xxxv. p. 62 (1918), and xxxvi. p. 36 of the same year; Mr. Jackson, xxxix. p. 294 and xl. p. 329 (1920); A. L. Narayan, xliii. p. 567 (1922).

‡ Wien, *Wied. Annal.* lxi. p. 151 (1897); Garbasso, *Vorlesungen über theoretische Spectroscopie*; Sellmeier, *Pogg. Ann.* cxlv. p. 538 (1872); and Oberbeck, *Wied. Ann.* xxxiv. p. 1041 (1888).

A and B (fig. 1), of two wooden laths, a and b , and of two bobs, P and Q, suspended to the laths by means of filaments

Fig. 1.

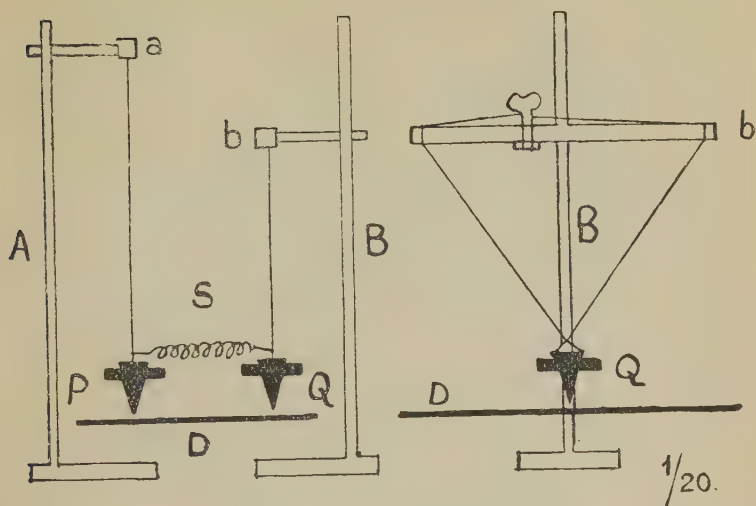
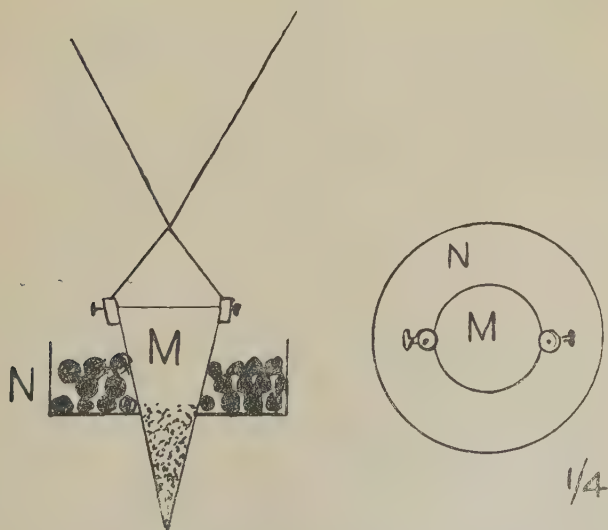


Fig. 2.



or thin wires. Due to such a manner of suspension very good, clear vibrations in the desired plane may be obtained without any difficulty. The bob is represented on fig. 2.

The tin funnel M is soldered to the cylindrical tub N, made of the same material. The funnels are filled with sand coloured by methylene-blue and the tubs with shot or any substitute. Coupling is performed by means of the spring S, which may be easily replaced. Both bobs are situated in the same horizontal plane, also in the case of different lengths, so that sand traces may be always obtained on a single moving board D. The perspective view of the whole arrangement is shown on Plate XVIII.

Let l_1 and l_2 be lengths, m_1 and m_2 masses, S_1 and S_2 linear displacements of two pendulums P and Q respectively. Further, let k be the extension coefficient of the spring S expressed in $\frac{\text{dynes}}{\text{cm.}}$. Then, neglecting the friction, the differential equations of motion may be written for small oscillations as follows :

$$\left. \begin{aligned} m_1 \frac{d^2 S_1}{dt^2} + \left(m_1 \frac{g}{l_1} + k \right) S_1 &= k S_2, \\ m_2 \frac{d^2 S_2}{dt^2} + \left(m_2 \frac{g}{l_2} + k \right) S_2 &= k S_1. \end{aligned} \right\} \dots \dots (1)$$

Or, putting

$$\frac{k}{m_1} = k_1, \quad \frac{k}{m_2} = k_2, \quad \text{and} \quad \frac{k}{m_1} + \frac{g}{l_1} = P_1^2, \quad \frac{k}{m_2} + \frac{g}{l_2} = P_2^2,$$

which are the frequencies of the first and of the second pendulums *when connected with the spring*, if the second and the first bobs respectively are fastened immovably,

$$\left. \begin{aligned} \frac{d^2 S_1}{dt^2} + P_1^2 S_1 &= k_1 S_1, \\ \frac{d^2 S_2}{dt^2} + P_2^2 S_2 &= k_2 S_1. \end{aligned} \right\} \dots \dots (2)$$

The coefficient of coupling is given by

$$\gamma^2 = \frac{k_1 k_2}{P_1^2 P_2^2} \dots \dots \dots (3)$$

With a corresponding spring (or wire) γ may be increased to 100 per cent.*

* In all the models here described it is practically impossible to obtain the coupling greater than 50-60 per cent.

Solving the equations (2) in the ordinary way, we obtain the general solution

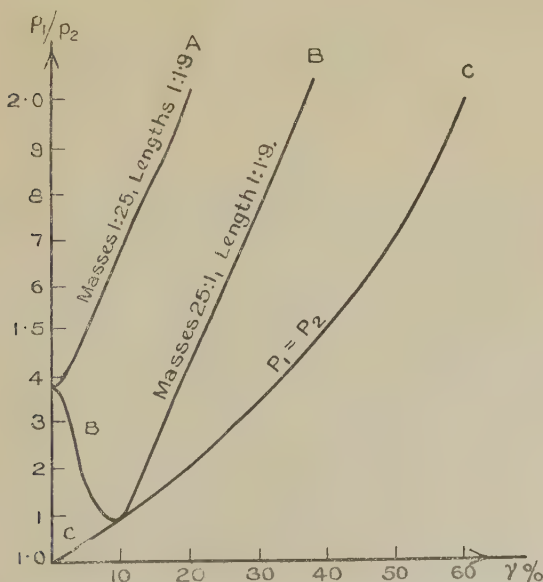
$$\left. \begin{aligned} S_1 &= A_1 \sin(p_1 t + \alpha_1) + A_2 \sin(p_2 t + \alpha_2), \\ S_2 &= \frac{P_1^2 - p_1^2}{k_1} A_1 \sin(p_1 t + \alpha_1) + \frac{P_1^2 - p_1^2}{k_1} A_2 \sin(p_2 t + \alpha_2), \end{aligned} \right\} (4)$$

where $A_1, A_2, \alpha_1, \alpha_2$ are arbitrary constants and p_1 and p_2 are given by

$$\left. \begin{aligned} 2p_1^2 &= P_1^2 + P_2^2 + \sqrt{(P_1^2 - P_2^2)^2 + 4k_1 k_2}, \\ 2p_2^2 &= P_1^2 + P_2^2 - \sqrt{(P_1^2 - P_2^2)^2 + 4k_1 k_2}. \end{aligned} \right\} \quad (5)$$

The relations among the ratio of frequencies $\frac{p_1}{p_2}$ and γ are graphically represented on fig. 3, showing the difference

Fig. 3.



between the cases when the heavy bob is on the long pendulum (graph A) or on the short one (graph B), just as in the double-cord model*. When $P_1 = P_2$, $\frac{p_1}{p_2}$ may be expressed in terms of γ :

$$\frac{p_1}{p_2} = \sqrt{\frac{1+\gamma}{1-\gamma}}, \quad \dots \quad (6)$$

just the same formula as for two magnetically or electrically-coupled circuits with equal periods (graph C).

Introducing the initial conditions in the equations (4) and in the differentiations of these with respect to time, we may find the solution for every special case. But we shall confine ourselves in this paper to the case of a single displacement.

Then for $t = 0$, $s_1 = S_0$, $s_2 = 0$, $\frac{ds_1}{dt} = \frac{ds_2}{dt} = 0$, and the special solution will be

$$\left. \begin{aligned} s_1 &= S_0 \frac{P_1^2 - p_2^2}{p_1^2 - p_2^2} \cos p_1 t - S_0 \frac{P_1^2 - p_1^2}{p_1^2 - p_2^2} \cos p_2 t, \\ s_2 &= S_0 \frac{(P_1^2 - p_1^2)(P_1^2 - p_2^2)}{k_1(p_1^2 - p_2^2)} (\cos p_1 t - \cos p_2 t). \end{aligned} \right\} \quad (7)$$

In the case of resonance ($P_1 = P_2 = P$) these may be rewritten as follows :

$$\left. \begin{aligned} s_1 &= \frac{1}{2} S_0 (\cos p_1 t + \cos p_2 t), \\ s_2 &= \frac{1}{2} S_0 \sqrt{\frac{m_1}{m_2}} (\cos p_1 t - \cos p_2 t), \end{aligned} \right\} \quad \cdot \cdot \quad (8)$$

where

$$\text{and} \quad \left. \begin{aligned} p_1^2 &= P^2(1 + \gamma) \\ p_2^2 &= P^2(1 - \gamma) \end{aligned} \right\} \quad \cdot \cdot \cdot \quad (9)$$

When the lengths of pendulums are equal ($l_1 = l_2$) (7) becomes

$$\left. \begin{aligned} s_1 &= \frac{m_2}{m_1 + m_2} s_0 \cos p_1 t + \frac{m_1}{m_1 + m_2} s_0 \cos p_2 t, \\ s_2 &= \frac{m_1}{m_1 + m_2} s_0 (\cos p_1 t - \cos p_2 t), \end{aligned} \right\} \quad \cdot \quad (10)$$

where

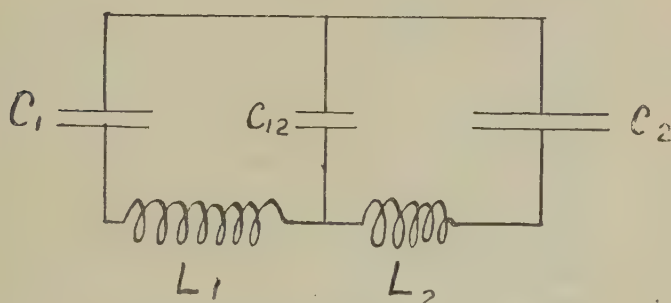
$$\left. \begin{aligned} p_1^2 &= P_1^2 + k_2, \\ p_2^2 &= P_2^2 - k_2. \end{aligned} \right\} \quad \cdot \cdot \cdot \quad (11)$$

In the case of electrically-coupled circuits (fig. 4) the equations of motion are in the usual notation :

$$\left. \begin{aligned} L_1 \frac{d^2 l_1}{dt^2} + \left(\frac{1}{C_1} + \frac{1}{C_{12}} \right) l_1 &= \frac{1}{C_{12}} l_2, \\ L_2 \frac{d^2 l_2}{dt^2} + \left(\frac{1}{C_2} + \frac{1}{C_{12}} \right) l_2 &= \frac{1}{C_{12}} l_1. \end{aligned} \right\} \quad \cdot \cdot \quad (12)$$

It is clear that these equations are identical with (1). Indeed, the dimensions of the respective coefficients are exactly the same if we put with Prof. Barton the inductances L_1 and L_2 analogous to the masses m_1 and m_2 , and the capacities C_1, C_2, C_{12} to the spring factors $\frac{l_1}{m_1 g}$, $\frac{l_2}{m_2 g}$, and $\frac{1}{k}$. (The dimension of $\frac{mg}{l}$ is just the same as of k , i. e., $\frac{\text{gr. cm.}}{\text{cm. sec.}^2}$).

Fig. 4.



So two pendulums* connected by a spring represent an exact analogy with electrically-coupled circuits. Moreover, they may be used to elucidate the case of inductive coupling with the same success as the models of Prof. Barton and Mr. Jackson, because the coupling in their models is also performed by means of displacement itself and not by means of its second differentiation. The simplicity of theory† and some little preferences of easiness and commodity of experimentation, make the described model suitable for laboratory work‡, as well as for demonstration use.

The above theory is illustrated here with a few curves only, because photographing is very dear in Russia. The curves Nos. 1–4 (Plate XIX.) are obtained with the pendulums of unequal lengths ($l_1 : l_2$ about 1 : 2), Nos. 5–8 (Plate XX.) with equal lengths; Nos. 2–4 illustrate the formula (8) and

* Or two springs, in which case k_1 and k_2 , their extension coefficients, must be put into the equations (1) instead of $\frac{m_1 g}{l_1}$ and $\frac{m_2 g}{l_2}$, but then experimental adjustment is more difficult and the damping is larger.

† Look at the contrast between (1) of this work and (27) and (28) of the first and (9) and (10) of the third papers of Prof. Barton.

‡ In this case students' familiarity at least with the elements of theory seems to be necessary.

may be regarded as a mechanical analogy of Tesla's transformer; Nos. 7 and 8 relate to (9), in which case the pendulums are not interchangeable and show the effect of different initial conditions; Nos. 5 and 6 are obtained with equal masses and lengths, which is a special case of (8) and (10) simultaneously; No. 1 shows the general case (periods, lengths, and masses unequal). The couplings used are always given as percentages. The upper curves in all photographs with unequal masses relate to the heavier bob. The initial conditions are shown in most of the photographs by the sand traces which are plotted by the pendulums before starting. The damping was very small in these experiments and has therefore been neglected in the above theory. The case when it is large is reserved for a later paper.

In conclusion, I wish to express my sincere thanks to Prof. S. A. Artzibysheff for giving me the idea of this work and kindness in putting at my disposal the instruments of the laboratory, and Prof. J. P. Krawetz, to whom I am indebted for many valuable suggestions.

Physical Laboratory of University,
Irkutsk, Siberia.
July 20, 1924.

LXIII. *A New Vacuum Thermoelement.*

By Dr. W. J. H. MOLL and Dr. H. C. BURGER*.

IN the application of the thermoelement for measuring radiation, the advantage of enclosing the element in vacuo has often been enunciated, and determinations have frequently been made of how much the sensitivity is increased by removing the air. The gain in sensitivity varies considerably, according to differences in the form of the element and the properties of the metals used, but is often rather important (5 to 10 fold).

The sensitivity of a thermoelement of given components is determined by the temperature difference of both junctions for a given radiation striking one of them. If none of the energy received were lost, the temperature of the exposed junction would rise without limit; in reality an equilibrium will be reached in which the energy received is equal to that lost. In the case of thermoelements in air, the energy is led off: (1) by the air, (2) by conduction through the metals, (3) by radiation. A great gain of sensitivity caused by exhausting means only that loss through the air was predominant previously.

* Communicated by Prof. O. W. Richardson, M.A., D.Sc., F.R.S.



$$m_1 = 2900 \text{ g.}$$

$$l_1 = 49 \text{ cm.}$$

No. 1.

$$m_2 = 725 \text{ g.}$$

$$l_2 = 92 \text{ cm.}$$

$$k = 3420 \frac{\text{d.}}{\text{cm.}}$$

$$m_1 = 2916 \text{ g.}$$

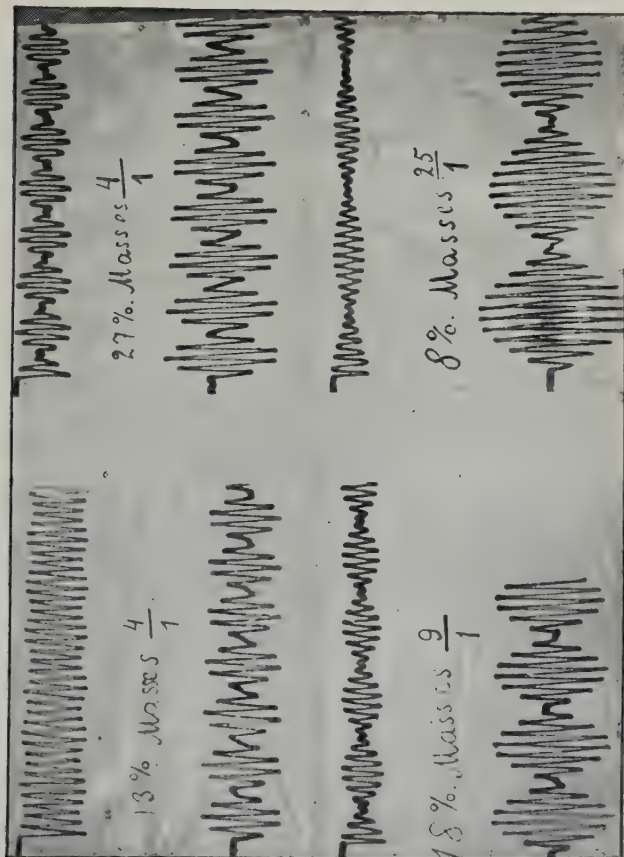
$$l_1 = 49 \text{ cm.}$$

No. 3.

$$m_2 = 324 \text{ g.}$$

$$l_2 = 92 \text{ cm.}$$

$$k = 1140 \frac{\text{d.}}{\text{cm.}}$$



$$m_1 = 2900 \text{ g.}$$

$$l_1 = 49 \text{ cm.}$$

No. 2.

$$m_2 = 725 \text{ g.}$$

$$l_2 = 92 \text{ cm.}$$

$$k = 9170 \frac{\text{d.}}{\text{cm.}}$$

$$m_1 = 2850 \text{ g.}$$

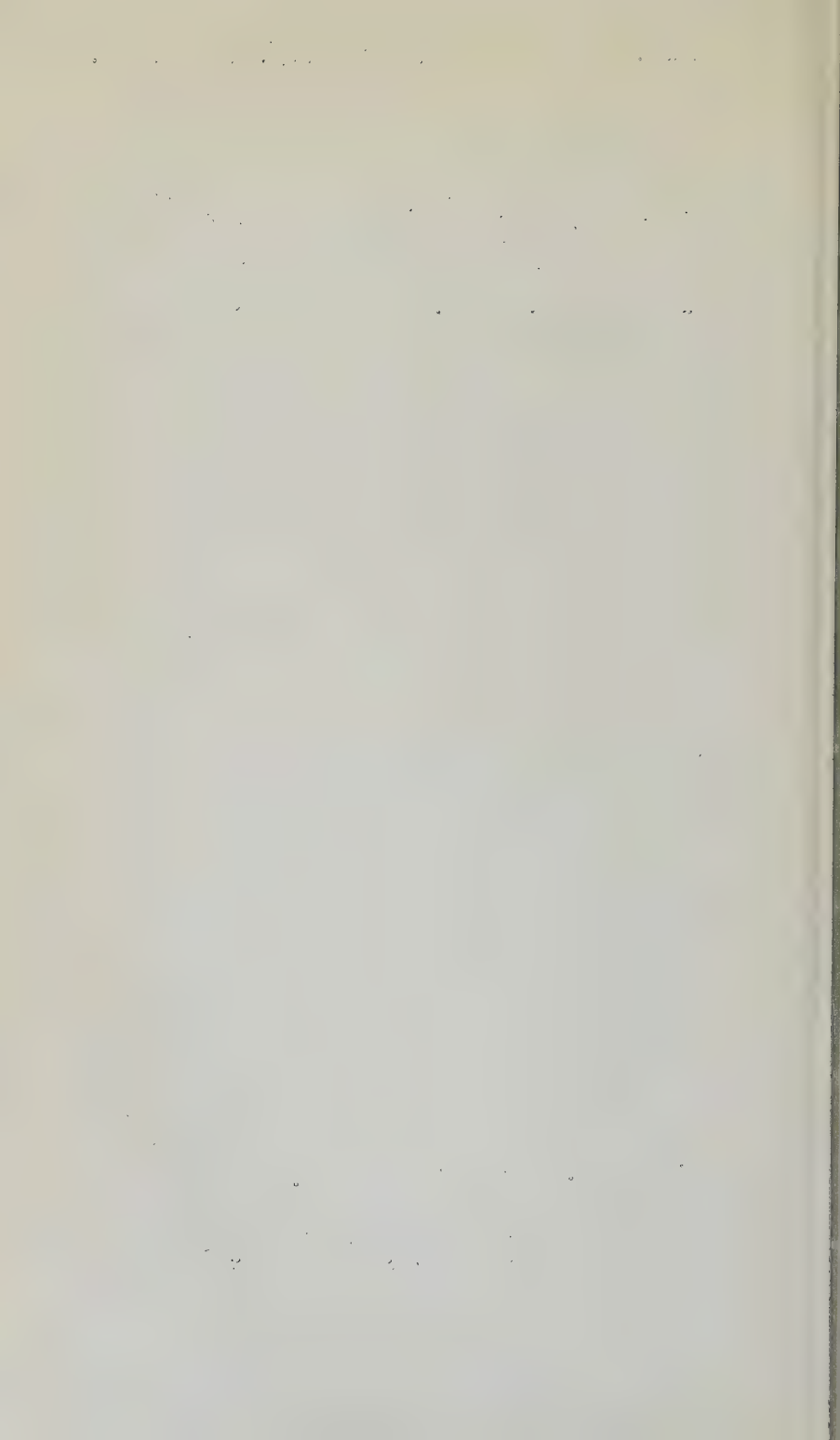
$$l_1 = 49 \text{ cm.}$$

No. 4.

$$m_2 = 114 \text{ g.}$$

$$l_2 = 92 \text{ cm.}$$

$$k = 1140 \frac{\text{d.}}{\text{cm.}}$$



$m_1 = 1530$ g.
 $l_1 = 93$ cm.

No. 5

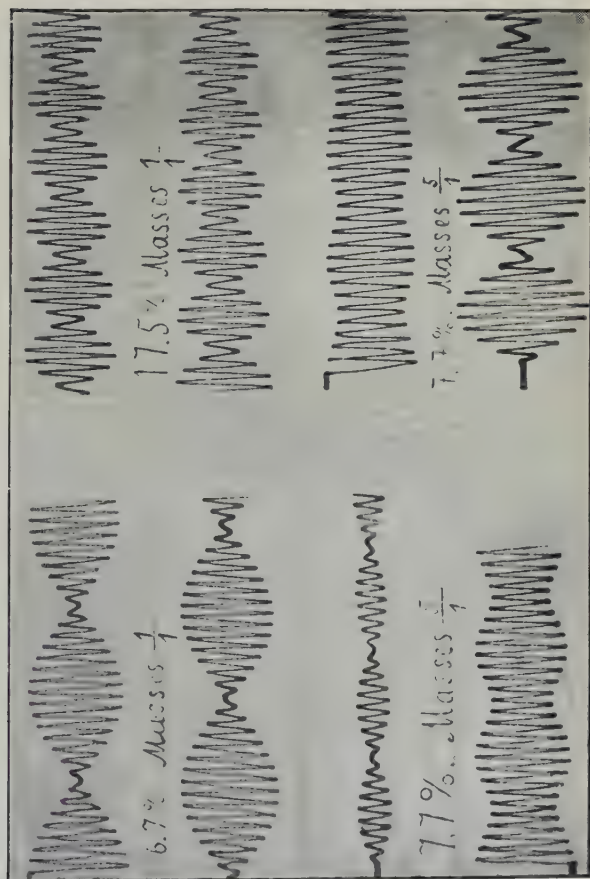
$m_2 = 1530$ g.
 $l_2 = 93$ cm.
 $k = 1140 \frac{d.}{cm.}$

$m_2 = 2700$ g.

$l_2 = 93$ cm.

No. 7.

$m_1 = 540$ g.
 $l_1 = 93$ cm.
 $k = 1140 \frac{d.}{cm.}$



$m_1 = 500$ g.
 $l_1 = 92$ cm.

No. 6.

$m_2 = 500$ g.
 $l_2 = 92$ cm.
 $k = 1140 \frac{d.}{cm.}$

$m_1 = 2700$ g.

$l_1 = 93$ cm.

No. 8.

$m_2 = 540$ g.
 $l_2 = 93$ cm.
 $k = 1140 \frac{d.}{cm.}$

The sensitivity of a vacuum-element of given components depends wholly on the heat conduction through the metals. The energy lost by conduction must be minimal, or better must be small as compared with the unavoidable loss by radiation. When this is the case, the effect of exhausting may become enormous. In our vacuum-elements the sensitivity is about 300 times as great as in air. A decrease of the leading away of the heat by conduction, however, implies an increase of the electrical resistance, and therefore should not be exaggerated. There will exist a *conditio optima*, i. e., the resistance of the thermoelement must be adapted to that of the galvanometer which is used to indicate the thermoelectric current. Anyhow there will exist for given components an ideal sensitivity of the thermoelement, an impassable limit, where the only loss of energy is through radiation.

This ideal sensitivity, viz. the case of equilibrium of radiation, may be computed easily for a given combination of metals.

Let d be the thickness of the receiver, O its area, r_1 and r_2 the mean reflecting power of front and back surfaces, c the specific heat and ρ the density of the material from which the receiver is made, I the radiation (in cal. per cm.² and per sec.), T the absolute temperature of the receiver, and σ the constant of radiation = 1.38×10^{-12} cal./cm.² sec.

Then the constant of external thermal conduction h is

$$h = (1 - r_1 + 1 - r_2) \cdot 4\sigma T^3.$$

The energy received per sec. = $I \cdot O \cdot (1 - r_1)$.

The energy lost per sec. = $h \cdot O \cdot \Delta T$,

if ΔT is the temperature difference between the element and the surroundings. This difference is a consequence of the radiation received.

The condition of equilibrium is

$$I \cdot O \cdot (1 - r_1) = h \cdot O \cdot \Delta T,$$

or

$$\Delta T = \frac{I (1 - r_1)}{h}.$$

In order to derive the sensitivity, let p be the thermoelectric power of the combination in volts, then the electromotive force E of the thermoelement is

$$E = \frac{I \cdot (1 - r_1) \cdot p}{h},$$

and its ideal sensitivity $S = \frac{E}{I} = \frac{1 - r_1}{h} p$.

For a given thermocouple the ideal sensitivity may thus be computed, and one can compare this figure with the real sensitivity found by experiment. In this way one has a good knowledge of how far the loss of energy by conduction (and eventually through the air) is negligible.

As a matter of course it is also possible to compute the decrease of sensitivity caused in a vacuum-element by conduction, when the dimensions and the heat conductivity of both metals are known. From such computations we got the conviction that it must be possible to approximate to the ideal sensitivity rather closely.

The ordinary method of constructing thermoelements implies a fairly good heat conduction. The best elements consist of a silver wire and a quite thin rod of bismuth, soldered together with an alloy of low melting-point. Silver has a high conductivity, the bismuth part has a cross-section which is relatively quite large. As the length of these elements was limited by practical reasons, the loss of energy by conduction was by no means negligible.

The usual method of construction involves moreover another and more serious disadvantage. The quickness of response of such elements even in contact with the air is rather poor. When now the air is expelled, and accordingly the sensitivity increased, the slowness of the apparatus becomes uncanny. The great heat-capacity of the element and especially of the solder is responsible for this.

As we proceeded with the construction of our vacuum-thermoelement, we were convinced that the direction in which we had to improve the element was to reduce the thickness of the metals, the solder, and the receiver to a minimum. This measure would have the advantage of decreasing the heat-conduction and thus increase the sensitivity, and at the same time would improve the quickness.

As to the quickness attainable, it could be estimated beforehand. The computation of the quickness of a thermoelement becomes somewhat uncertain if the loss of energy by conduction plays a predominant part, since in that case the notion of quickness is indefinite. It is possible, for instance, that with a thermoelement 50 per cent. of the final electromotive force is reached quite rapidly, while it takes a very long time before 99 per cent. of this final value is attained. But since we expected to obtain almost the condition of equilibrium of radiation, a computation on the premise of a heat-conduction zero would mean a fair approximation.

For that case (no other loss of energy than by radiation), the quickness of the thermoelement may be derived from a simple calculation. Using the same symbols as above, we will consider a thermoelement, exposed to radiation for some time, the radiation being intercepted at a given time $t=0$, and calculate the rate at which the temperature-difference between the element and the surroundings falls off. The temperature-difference existing at a time t will be expressed by

$$\Delta T \cdot e^{-\frac{t}{t_0}}$$

where

$$t_0 = \frac{d \cdot \rho \cdot c}{(1-r_1+1-r_2) \cdot 4\sigma T^3}$$

Now the "quickness" of the thermoelement may be defined as the time θ elapsing before ΔT has attained 1 per cent. of its initial value. As $e^{-\frac{\theta}{t_0}} = 0.01$ means $\theta = 4.38 t_0$,

$$\theta = 4.38 \frac{d \cdot \rho \cdot c}{(1-r_1+1-r_2) \cdot 4\sigma T^3}$$

In order to give a numerical example, we will apply this formula to the new thermoelement described further on. Of one of these elements the constants were approximately $d = 1.1 \times 10^{-4}$, $\rho = 8.5$, $c = 0.097$, $r_1 = 0.10$, $r_2 = 0.70$, $T = 300$.

The computed "quickness" θ is 2.3 sec., a value which is in fair agreement with that given by experiment.

Before we proceed to a detailed description of the new thermoelement, we will lay stress upon what in our eyes is a great advantage of the vacuum. The presence of air may give rise to unexpected and annoying perturbances. As a matter of fact, slight adiabatic variations of the air pressure change the temperature of a junction, especially if its heat-capacity is small. Besides one has ever to be apprehensive of convection of the air surrounding the element, brought about by outside circumstances. By a sufficiently high vacuum these errors are avoided, and the reliability of the instrument is greatly increased.

In order to minimize the heat conduction and at the same time the heat capacity of the thermoelement, we made use of the so-called thermofoil, described elsewhere*. This material is constructed in the following way. Two rather thick plates (*e.g.* of manganin and constantan) are soldered

* Proc. of the London Phys. Soc. xxxv. p. 258 (1923).

together with silver. The superfluous silver is polished away, after which a narrow seam of silver remains. The bimetallic plate is then rolled out in the direction of the seam. In this process the seam is practically not broadened, and it has been found possible to prepare in this way a quite thin foil, consisting of two sheets of metal connected by a silver seam, the silver having the same thickness as the metals. By simply cutting this thermofoil into narrow strips, a large number of thermoelements is obtained.

These elements are applied in the construction of the thermopiles which have been described by one of us. The thickness of the elements was about 0.005 mm. The quickness of these piles (an equilibrium is reached within 2 seconds) is to a great part due to the effective heat transport by means of the air between the strips and a heavy plate of copper.

If such a thermopile is evacuated, its sensitivity increases considerably, but at the same time it loses its quickness. We commenced our investigations with an element of 0.005 mm. thickness and 15 mm. long. It needed 12 seconds to come to equilibrium. As compared with other vacuum thermoelements this result was not bad*, but we aimed at a quickness of the same order as was attained with the thermopiles mentioned above.

We now tried to refine the process of rolling out, and with much care and a great loss of material we succeeded in preparing small pieces of thermofoil with a thickness of only 0.001 mm.

Fig. 1.

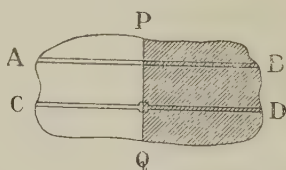


Fig. 1 represents a piece of thermofoil on an enlarged scale. PQ is the narrow seam of solder. A strip AB cut

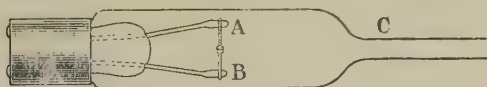
* There exists in the literature a communication about a vacuum thermoelement with a formidable quickness. Pettit and Nicholson (Astroph. Journ. lvi. p. 295 (1922)) prove by calculation that their element has a quickness of 0.006 sec.! They made a mistake in their reasoning. An experiment would have shown that the quickness of this element is of the order of 30 sec.

from this foil forms a linear element*. For some applications it was desirable to have a receiving area of greater extension, and for that purpose we constructed elements of the form C D. It will be clear that cutting such elements would be practically impossible. We succeeded by covering the whole back surface of the foil and on the front only the part C D with a varnish, and dissolving the surrounding foil in nitric acid.

One side of the sensitive part of the thermoelement had to be blackened. Soot was inappropriate for this purpose, as its heat conduction *in vacuo* is too small. We applied an aqueous solution of colloidal carbon, spread out in a layer of about 0.001 mm. thickness.

An element of one or the other form is now mounted within a glass tube, in the same manner as is usual in the construction of electric lamps. The two electrodes are heavy wires, and the element is soldered at A and B (see fig. 2). The narrow part of the tube is connected to a

Fig. 2.



high-vacuum pump, and the evacuated thermoelement is heated during an hour to 300° C. in order to expel all gas residues from the glass and the metal parts. Mercury vapour and other impurities are frozen out with liquid air, and finally the tube is melted off at C.

The heating during the evacuation is necessary as without this precaution the vacuum is not durable. With the older types of thermoelements this heating was impossible, since the solder used had too low a melting-point. The thermofoil, however, is soldered with silver and sustains a heating to 400°.

The sensitivity, the quickness, etc. of these thermoelements differs somewhat for the various specimens. But we will mention some average data, in order to give an impression of the features of the instrument.

The sensitivity of the element with an extended junction (of form C D, see fig. 1) is from 50 to 70 per cent. of the ideal. The linear elements have a relatively greater heat

* Such an element of 0.05 mm. breadth and 8 mm. length has a resistance of 15 ohms, and weighs only 0.003 milligram.

conduction, though even in this case the loss through conduction is not much greater than that through radiation. An element of form $\bar{C}D$, with a receiving area of 1 mm.^2 , required $\frac{1}{15} \cdot 10^{-6} \text{ cal. sec.}^{-1}$ for giving 1 microvolt. A linear element of 0.05 breadth, when receiving radiation from the same source as the former one, and along the same length of 1 mm., gives only $\frac{1}{3}$ microvolt. But as compared with the former thermoelement, the receiving area of the linear one is only $\frac{1}{20} \text{ mm.}^2$. Accordingly it needs only $\frac{1}{20} \cdot \frac{1}{15} \cdot 10^{-6} \text{ cal. sec.}^{-1}$ to give $\frac{1}{3}$ microvolt, *i.e.* $10^{-8} \text{ cal. sec.}^{-1}$ per microvolt.

The mean error of the galvanometer we used was $\frac{1}{1000}$ microvolt, corresponding to less than $\frac{1}{2000}$ erg per sec.

The quickness of response is quite satisfactory. When radiation is admitted, the element reaches its final temperature within two or three seconds.

The resistance of these thermoelements is about 10 to 20 ohms.

Physical Laboratory
of the University.
Utrecht, June 1925.

LXIV. *The Thermo-Relay.* By DR. W. J. H. MOLL
and DR. H. C. BURGER *.

TO measure a small angle through which a body rotates, use is very frequently made of a little mirror fixed to the body, the mirror reflecting a beam of light, and projecting a spot (provided with an index) on to a scale. The great advantage of this method lies in the possibility of using a large scale distance, and therefore getting great displacements of the spot for relatively small rotations. But it is of no use to exaggerate this distance. Enlarging the scale distance above a certain limit yields for a given rotation a greater displacement it is true, but the sharpness of the index is worse, and the accuracy obtained remains practically the same. It is for the same reason that a scale is never subdivided in tenths of a mm. and the spot read off with a magnifying glass; if magnified, the image loses its sharpness and no gain in accuracy would have been reached. As a matter of fact, in all measurements of this sort the accuracy attainable is limited by the defective sharpness of the light-index.

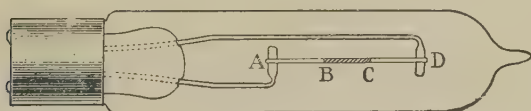
* Communicated by Prof. O. W. Richardson, M.A., D.Sc., F.R.S.

In the following lines we will describe a simple method of measuring rotations so small as to be unmeasurable in the usual way. This method makes use of the above-mentioned reflecting mirror, but its accuracy is absolutely independent of the sharpness of the spot. It may even be applied in connexion with a mirror of quite bad quality. Moreover, it permits a photographic registration

The principle of the new method is the generating of a thermo-electric current by means of the spot of light. This current is indicated by a galvanometer, and the deflexions may either be read off or recorded photographically on a registering drum.

The new apparatus (the thermo-relay) is constructed in the following way. From a piece of "thermofoil"*) a strip ABCD (fig. 1.) is cut out. The parts AB and CD are of

Fig. 1.



constantan, the part BC of manganin. This strip is blackened and mounted in an evacuated glass vessel, in the same manner as is usual in the construction of electric lamps. The thermo-relay is enclosed in a double brass tube provided with slits in front of the strip.

When now a spot (sharp or unsharp) is projected upon the middle part of the strip, both junctions will be heated, and a galvanometer connected to the relay will show a deflexion. By shifting the relay in the direction of the strip, this deflexion can be made zero, both junctions having then the same temperature. A small rotation of the mirror which gives a displacement of the spot, *e. g.* to the right, will raise the temperature of the right junction above that of the left, and will cause a galvanometer deflexion. A rotation of the mirror in the other direction will give an opposite deflexion. If the displacements of the spot are not too great, the galvanometer deflexion is proportional to the rotation.

It is a matter of course that the source of light must have an invariable intensity. An incandescent lamp with short spiral connected to some accumulators will do perfectly well. If the mirror is small, it is advisable to use the

* *Suprà*, p. 618.

following arrangement. The spiral of the lamp is projected by a lens on to the little mirror ; a second lens, placed in front of the mirror, converges the reflected beam of light, and a cylindrical lens, placed in front of the slit of the brass tube, makes an elongated image of the mirror on the strip. The thermo-currents generated by an arrangement of this sort will be strong enough for most applications. With an incandescent lamp of 16 candles, a mirror of only 5 mm. diameter, and a good coil-galvanometer, a rotation of the mirror through an angle of $\frac{1}{10}$ sec. gives a measurable galvanometer deflexion.

This very high sensitivity of the thermo-relay is due to the fact that there is no loss of energy through the air, and that the loss by conduction along the very thin strips (thickness about 0.001 mm.) is quite small. The vacuum excludes, moreover, all disturbances which would arise if the strip were surrounded by air, and consequently the thermo-relay is practically free from perturbations. If necessary, it can be used in connexion with a very sensitive galvanometer.

A second advantage of the extreme thinness of the strip is the quickness in response of the thermo-relay. In combination with a quick and aperiodic galvanometer, a deflexion reaches its final value within three seconds.

One of the applications of the thermo-relay will be described in the following paper, viz. the amplification of the sensitivity of a galvanometer. It will be shown there that a tenfold or a hundredfold amplification can easily be reached by throwing the spot reflected by the galvanometer mirror on a thermo-relay, and connecting the relay to a second galvanometer.

Physical Laboratory
of the University.
Utrecht, June 1925.

LXV. *The Sensitivity of a Galvanometer and its Amplification.*
By Dr. W. J. H. MOLL and Dr H. C. BURGER*.

AN important property of the galvanometer is its sensitivity. For most applications it is the volt-sensitivity that matters—that is to say, the deflexion on a scale at one metre for one microvolt. The importance of this figure, however, is generally over-estimated. In all publications about investigations where the highest achievements of the galvanometer are wanted, this figure is

* Communicated by Prof. O. W. Richardson M.A., D.Sc., F.R.S.

mentioned as its most salient feature ; in the construction of a new galvanometer the main object is usually to attain an extreme sensitivity.

Yet it will be evident that the essential feature of a galvanometer intended for the study of the weakest effects is not the bigness of the deflexion for one microvolt, but the smallness of the electromotive force which can be read off with certainty. It is true that the latter specification is not independent of the conditions under which the galvanometer is used, and that therefore it is necessary to detail these conditions ; a reference, on the other hand, to the mere sensitivity has for practical purposes no value at all. In all galvanometer work one has to struggle with disturbances. A galvanometer with a high sensitivity, but strongly subject to perturbations, will be of little use for the measurement of small electromotive forces.

The disturbances which limit in practice the efficiency of a galvanometer may be divided into two kinds : disturbances peculiar to the galvanometer as such, and those acting in the outer circuit. The first are dependent in a high degree on the place where the apparatus has been installed ; but under the same circumstances of location various galvanometers are affected by perturbations to a quite different degree, and thus the necessity presents itself of characterizing the quality of the galvanometer in this respect. For this purpose one could proceed in the following way. The galvanometer in question is installed in a cellar-vault, placed on a wall-bracket or suspended, and short-circuited. During the night one observes the zero, and an estimation is made of the mean deviation. When the sensitivity of the galvanometer is known, one can derive from these observations the mean error, expressed in microvolts, of the galvanometer under most favourable conditions. This mean error has to be considered as the most valuable information about the galvanometer.

As compared with the disturbances met with by the galvanometer itself, those originating in the outer circuit are usually predominant. In so far as they have a regular course, they may be taken into account ; a skilled experimenter can take account as well of suddenly arising perturbations. There remains, however, a mean error resulting from the outer disturbances, which frequently is much greater than that peculiar to the short-circuited galvanometer.

Now the amount of this mean error is *ceteris paribus* not the same for different galvanometers. In this respect the

quickness of the galvanometer plays an important part which is usually under-estimated. While a very slow apparatus integrates the various disturbing effects, it often becomes possible with a quick one to discover disturbances of short period. Once recognized as such, they may be taken into account.

There is still another reason why with a quick galvanometer the mean error caused by disturbances in the outer circuit may be made smaller than would be possible with a slow one. With a sufficiently quick apparatus it is possible to distinguish the different disturbances from each other. The closing of a door, the passing in the street of a carriage, currents caused by induction by a faulty insulation or a bad contact, thermo-currents, etc.—all give their characteristic fluctuations of the spot. The differences in their aspect appear in a striking manner when the fluctuations of the spot of a quick galvanometer are registered. Not infrequently one succeeds in tracing in this manner the presence of known and unknown disturbances, and can then exclude them.

We think, therefore, that the efficiency of a galvanometer for the study of weak effects should not be judged by its sensitivity. The mean error, expressed in microvolts, of the galvanometer when short-circuited and installed under the most favourable conditions is one criterion, and the galvanometer's quickness is the second.

It is possible to amplify the sensitivity of a galvanometer by means of a "thermo-relay *".

A beam of light, emerging from a little incandescent lamp, is reflected by the mirror of the galvanometer and thrown on a thermo-element of special construction; it generates a thermo-current, which is indicated by an auxiliary galvanometer. The size of amplification depends on the intensity of the spot projected on the thermo-relay, and can be adjusted at will by regulating the lamp's current. Even with a galvanometer-mirror of small dimensions (*e.g.* 5 mm. diameter) it is easy to attain a hundred-fold amplification.

When this method is applied to one of the usual very sensitive galvanometers, an enormous sensitivity may be reached. The proceeding, however, as a rule has no meaning, because the errors are magnified to the same amount, and the mean error expressed in microvolts usually

* *Suprà*, p. 624.

remains the same. The method will give only a real advance if used in combination with a galvanometer the zero of which is so steady that the irregular fluctuations of the spot are smaller than the least readable deflexions.

We investigated the efficiency of this method of amplification with a coil-galvanometer of special construction, designed by one of us *. Its great zero-steadiness is principally due to the fact that the coil is not suspended as is usual, but stretched between two wires. When used in the ordinary way, and giving a spot on a scale at one metre, readings can be made with a precision of $\frac{1}{10}$ or $\frac{1}{20}$ mm. Its steadiness would permit a reading to $\frac{1}{100}$ mm. and less; but even with the best mirror the precision of the reading is limited by the defective sharpness of the light-index. This galvanometer has a time of indication of less than two seconds; its resistance is about 50 ohms.

We installed the apparatus on a wall-bracket in a room on the second floor of our Institute, which is situated within the town and a short distance from the traffic. The outer circuit was formed by a resistance-box, by means of which small electromotive forces could be inserted.

Fig. 1 *a* gives a reproduction on a true scale of a photographic registration of the zero during eight minutes. Two minutes after beginning, an electromotive force of ten microvolts was inserted during ten seconds, and four minutes after that an electromotive force of one microvolt. The reading is certain to about $\frac{1}{20}$ mm., corresponding to a mean error of 25×10^{-9} volt.

Fig. 1 *b* gives the line when a 5-fold amplification had been applied. This curve has been recorded therefore by an auxiliary galvanometer, the latter being of the same type as the primary one. As is obvious from the picture, the quickness of response has become somewhat smaller, but the reading is still certain to $\frac{1}{20}$ mm. The mean error has been reduced to about 5×10^{-9} volt.

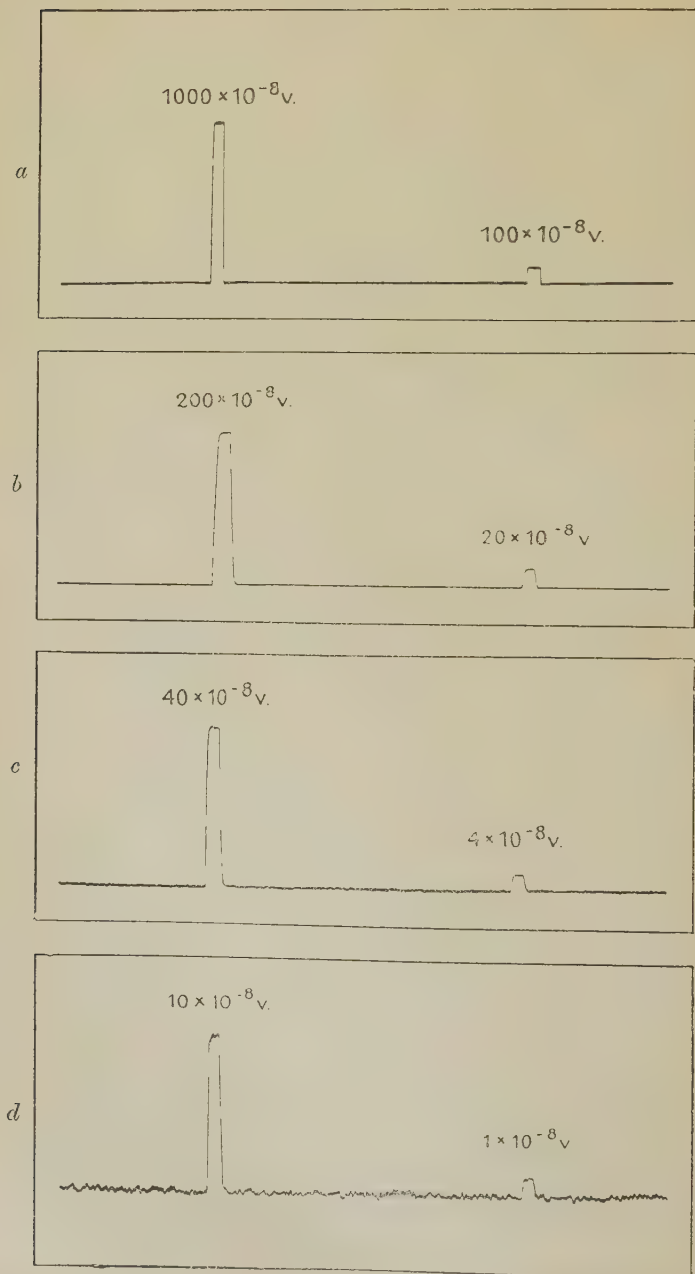
Fig. 1 *c* shows a 25-fold amplification of the sensitivity. The zero-line is no longer smooth; the error of reading has become greater, and amounts to about $\frac{1}{10}$ mm., corresponding to 2×10^{-9} volt.

When the sensitivity is still more amplified, the real progress is but small, as fig. 1 *d*, a 100-fold amplification, shows. The mean error is here about 1×10^{-9} volt. Further amplification of the sensitivity would be of no use.

The conspicuous disturbance, visible in this figure (fig. 1 *d*),

* Proc. Phys. Soc. xxxv. p. 253 (1923).

Fig. 1.



has been caused in all probability by microseismic perturbations. It has a period of about six seconds, and has the same character at daytime as in the night. That a slow motion to and fro of the walls entails rotations of the mirror must be a consequence of a slight asymmetry of the coil. We are hopeful to succeed in reducing this asymmetry, and to raise by that means the efficiency of our galvanometer still considerably.

That it has been possible to attain such a high sensitivity, and to overcome all other disturbances, is principally due to the quickness of our combination. Indeed, various perturbations became manifest as we gradually increased the sensitivity, but by recording the zero photographically they could be identified and eliminated one after the other.

Physical Laboratory
of the University.
Utrecht, June 1925.

LXVI. *The Piezo-Electric Oscillograph* *.

By A. B. Wood, D.Sc., F.Inst.P. †

[Plates XXI. & XXII.]

IN the February issue of the Philosophical Magazine an account is given by C. E. Wynn-Williams, M.Sc. (pp. 289-313) of a piezo-electric oscillograph. Mention is made of more or less unsuccessful attempts to utilize quartz strips for the purpose in view, but these have been abandoned as being too insensitive. Rochelle salt, on the other hand, is considerably more sensitive, but possesses certain disagreeable features mentioned in the paper. The paper concludes by a statement: "If sufficient magnification could be obtained a quartz oscillograph would probably, owing to the very definite physical properties of this substance, be superior to one of rochelle salt."

It is the object of this note now to point out that the quartz oscillograph is by no means so impracticable as might be supposed. In 1920 the author designed and tested two types of quartz strip oscillograph which gave very satisfactory results. A description of these instruments is given in Patent No. 180,787, March 1921, but it may not

* The oscillographs described were designed and constructed in 1920, and the paper is now published by permission of the Admiralty.

† Communicated by Mr. F. E. Smith, C.B.E., F.R.S.

be out of place to make further reference to them here. The two types will be described as the single-strip and the double-strip oscillographs*.

I. *Single-Strip Oscillograph.*

In principle, this is essentially the same as that described by Mr. Wynn-Williams (and illustrated in his paper in fig. 4, p. 296), but differs in important details. The strip of quartz is cut with its thickness ' e ' in the direction of the electric axis, its length ' l ' in the third direction, and its breadth ' b ' in the direction of the optic axis. When a p.d. of V electrostatic units is applied across the electric axis then the dilatation δ in the direction of its length is given by

$$\delta = K \frac{l}{e} V,$$

where K is a constant depending on the piezo-electric properties of the crystal.

In the case of quartz $K = 6.45 \times 10^{-8}$.

It will be seen that the change of length of the crystal is directly proportional to the applied voltage, and to the ratio of length to thickness. See Table I. In Mr. Williams's experiments a slab of crystal 5 cm. long and 0.3 cm. thick was employed, whence

$$\delta = 1.07 \times 10^{-6} V \text{ cm.},$$

or if V is expressed in volts,

$$\delta = 3.5 \times 10^{-9} V \text{ cm.};$$

i. e., for $V = 1000$ volts

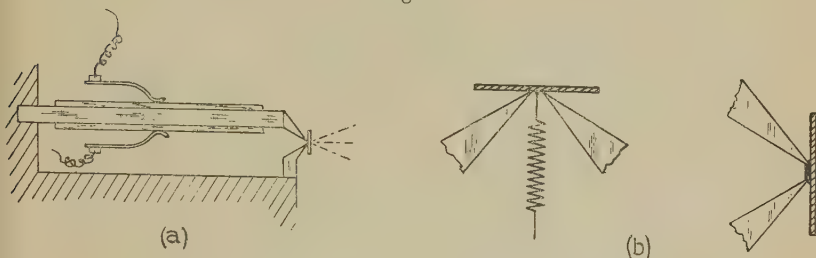
$$\delta = 3.5 \times 10^{-6} \text{ cm.}$$

This is a very small deflexion, but it is possible to increase it considerably. In the first place, by reducing the thickness of the slab from .3 cm. to .03 cm. the value of δ is multiplied 10 times. By means of a simple optical lever device, shown in fig. 1 a, the resulting dilatation of the slab may again be magnified 10^4 times. In the arrangement shown, an oscillograph mirror (about $.5 \times 1$ mm.) is pivoted on parallel knife-edges spaced about 0.1 mm. apart, and a spot of light reflected from it on a scale or on a photographic film at say 1 metre distance. One of the knife-edges is attached to the top of the slab, whilst the other is fixed firmly to the

* The properties of single and double piezo-electric strips, as utilized in the design of these Oscillographs, are described in 'Œuvres de Pierre Curie,' Paris (Gauthier Villars, 1908), pp. 35-55.

base of the oscillograph. The magnification factor of this arrangement is therefore $2 \times 100 / 0.01 = 2 \times 10^4$. Thus the deflexion ' d ' per 1000 volts will be $2 \times 10^4 \delta$, which becomes 0.43 cm. for a crystal slab of thickness 0.5 mm. An oscillograph constructed on this principle gave results in accordance with the theory. The mirror was held on the knife-edges by an elastic cement (see fig. 1b) (a spring would probably serve the same purpose).

Fig. 1.



Single-Strip Type.

It is to be noted that in this arrangement the inertia of the moving parts is very small, but it should be observed also that the force holding the mirror on the knife-edges must be considerable in order that the acceleration of the vibrating strip of quartz should never exceed that due to the restoring action of the spring. The natural frequency of this type of oscillograph is high, corresponding to the longitudinal vibration of the strip (if ' l ' = 5 cm. frequency 25,000 app.). The insulation is of course exceptionally good, and both positive and negative deflexions are strictly proportional to voltage. In these respects quartz is superior to rochelle salt.

II. *Double-Strip Oscillograph.*

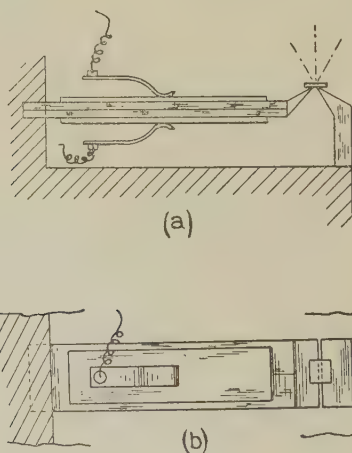
The sensitivity of the single-strip quartz oscillograph referred to above is inversely proportional to the thickness of the strip and directly proportional to the length. Limits are set to the former by the mechanical and electrical strength of the crystal, whilst the length is limited by the maximum size of crystals obtainable. By employing a device, well known in the study of thermal expansion, it is possible to increase still further the sensitivity of the quartz strip oscillograph. This is accomplished as follows. If two strips of crystal (of the nature just described) are cemented

together in opposite senses—so that one layer expands whilst the other contracts—the bi-plate assumes a curvature whose radius depends on the amount of dilatation. If ' l ' and ' e ' represent the length and thickness of each of the layers and V electrostatic units the p.d. applied to the outer faces, then the lateral displacement of the unclamped extremity of the compound strip will be

$$\delta = \frac{3}{4} K \cdot \frac{l^2}{e^2} \cdot V,$$

the method of mounting being illustrated in fig. 2 (sectional

Fig. 2.



Double-Strip Type.

elevation in *a*, plan in *b*). The dilatation is now proportional to the square of the ratio l/e —indicating a greatly increased sensitivity.

If quartz is used, $K = 6.45 \times 10^{-8}$. Taking $l = 5$ cm. and $e = 0.05$ cm.,

$$\delta = 1.6 \times 10^{-6} V \text{ cm. if } V \text{ is expressed in volts.}$$

With an optical magnification of 2×10^4 the deflexion ' d ' at 1 metre will be $.032 V$ cm., *i. e.* 0.32 mm. per volt.

It will at once be seen that this represents a very considerable increase in sensitivity over the single-strip type of oscillograph, in the example given the increase being in the ratio $\frac{3}{4} l/e$, *i. e.* 75 times. (See Table II.)

The natural frequency of this type is of necessity rather

low*, for now we are dealing with the transverse vibrations of the piezo-electric strip. The pronounced resonance is very apparent when an A.C. voltage of continuously variable frequency is applied. The band of light produced by the mirror oscillations widens out rapidly near resonance, and the strip itself emits a loud note corresponding to the applied frequency. This resonance can be reduced in several ways, one of the most simple depending on the choice of the medium for mounting the mirror on the knife-edges. Photographs of two early patterns of quartz oscillograph are shown in Pl. XXI. fig. 3—Single Strip (a), Double Strip (b).

With either type of oscillograph the dimensions of the crystal slab employed are determined by the voltage-range for which the instrument is to be used. The thinner the slab, the lower will be the voltage-range that it will detect.

The fact that crystals of rochelle salt show much greater piezo-electric effects than quartz was realized from the first, but owing to the somewhat irregular behaviour of rochelle salt as regards sensitiveness and insulation and its liability to breakdown under electric stress, it was considered desirable to develop the quartz type for metrical purposes.

The following tables are inserted as a convenient means of comparing the sensitivities of the single- and double-strip oscillographs, and to provide a basis of comparison with observations of the behaviour of the two oscillographs illustrated in fig. 3 a and b (Pl. XXI.).

TABLE I.

The table indicates the increase of sensitivity with the ratio length/thickness in the case of the *single-strip quartz oscillograph*.

Optical magnification assumed = 10^4 .

Length $l = 5$ cm.

K for quartz = 6.45×10^{-8} .

Thickness 'e' cm.	l/e	Sensitivity (at 1 metre).	
		cm. per volt.	Volts per cm.
0.5	10	2.15×10^{-5}	46500
.2	25	5.4×10^{-5}	18500
.1	50	1.07×10^{-4}	9350
.05	100	2.15×10^{-4}	4650
.02	250	5.4×10^{-4}	1850
.01	500	1.07×10^{-3}	935

* E. g. 1350 ~ /sec. in one oscillograph.

The single-strip oscillograph shown in fig. 3 *a* has a length of 5.1 cm., thickness .06 cm., i.e. $l/e = 85$. The deflexions obtained by the application of positive and negative potentials up to ± 6000 volts indicated a linear relation and a sensitivity of approximately 6000 volts per cm., which is in moderately good agreement with the tabulated values in Table I. The natural frequency of the oscillograph was not determined experimentally, but calculation indicates a value of the order of 20,000 \sim /sec.

In fig. 3 *c* is shown a single-strip rochelle salt oscillograph, the strip having a length of 5.2 cm., thickness 0.47 cm., whence $l/e = 10.6$. The D.C. sensitivity is approximately 10 volts per cm. at a metre, corresponding to about 4000 times the equivalent sensitivity of a quartz strip of the same dimensions. The natural frequency of the rochelle salt strip shown is between 3000 and 4000 \sim /sec.

TABLE II.

The table indicates the increase of sensitivity with the ratio length/thickness in the *double-strip or bi-plate quartz oscillograph*.

Optical magnification assumed = 10^4 .

Length $l = 5$ cm.

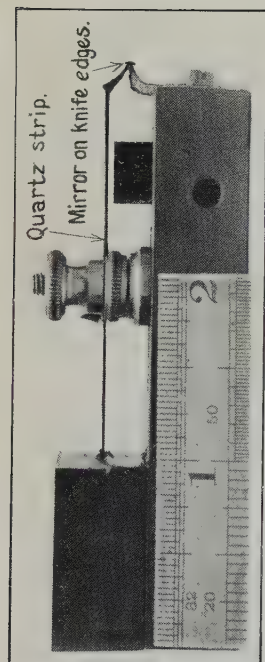
K for quartz = 6.45×10^{-8} .

Thickness 'e' cm.	l/e .	l^2/e^2 .	Sensitivity.	
			cm. per volt.	Volts per cm.
0.5	10	100	0.00016	6250
.2	25	625	.001	1000
.1	50	2500	.004	250
.05	100	10000	.016	62
.02	250	62500	.10	10
.01	500	250000	.4	2.5

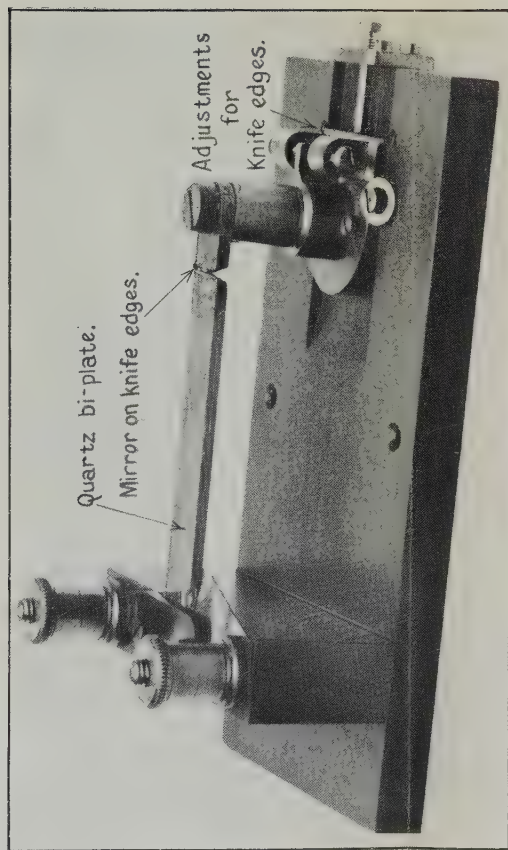
The double-strip oscillograph shown in fig. 3 *b* consists of two quartz plates each of length 5 cm., thickness .08 cm., i.e. the length/thickness ratio = 62.5.

As in the case of the single-strip type, the deflexions varied linearly with voltage, positive or negative, and a sensitivity of 170 volts per cm. at one metre was observed—in good agreement with values given in Table II. The natural frequency of this oscillograph was 1350 \sim /sec. approximately. When opportunity offers, it is proposed to

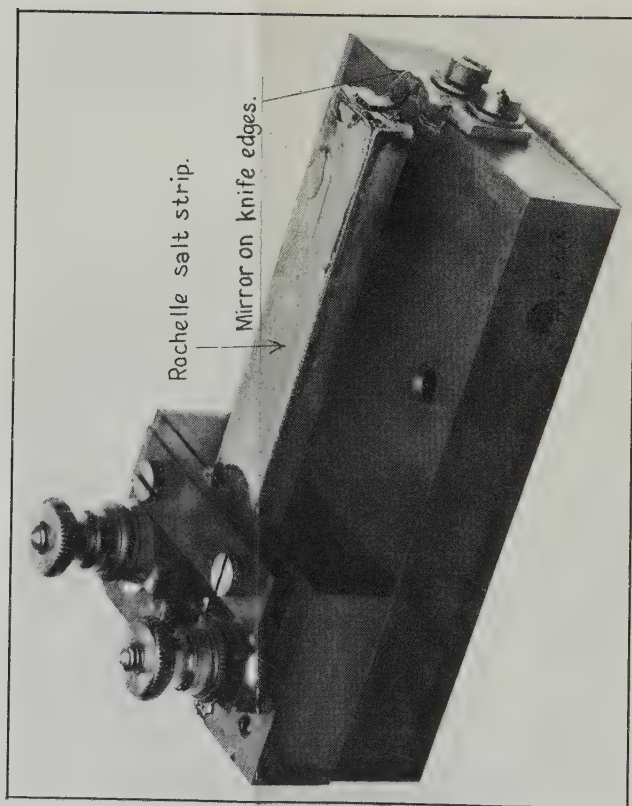
FIG. 3.



a. Single-Strip Quartz Oscillograph.

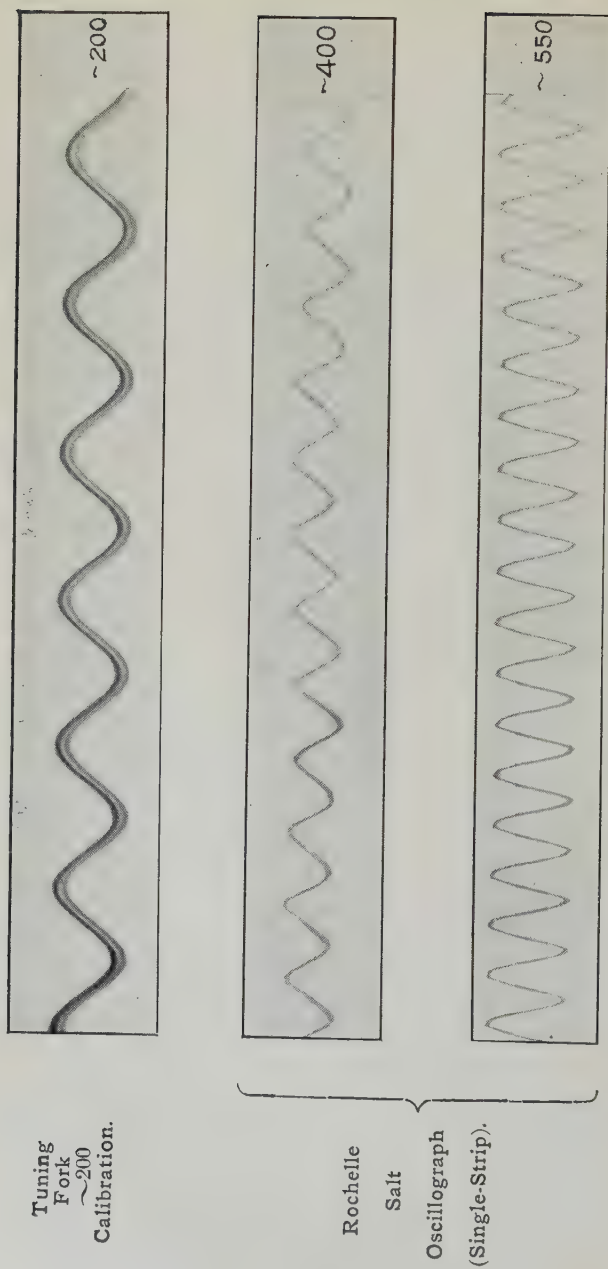


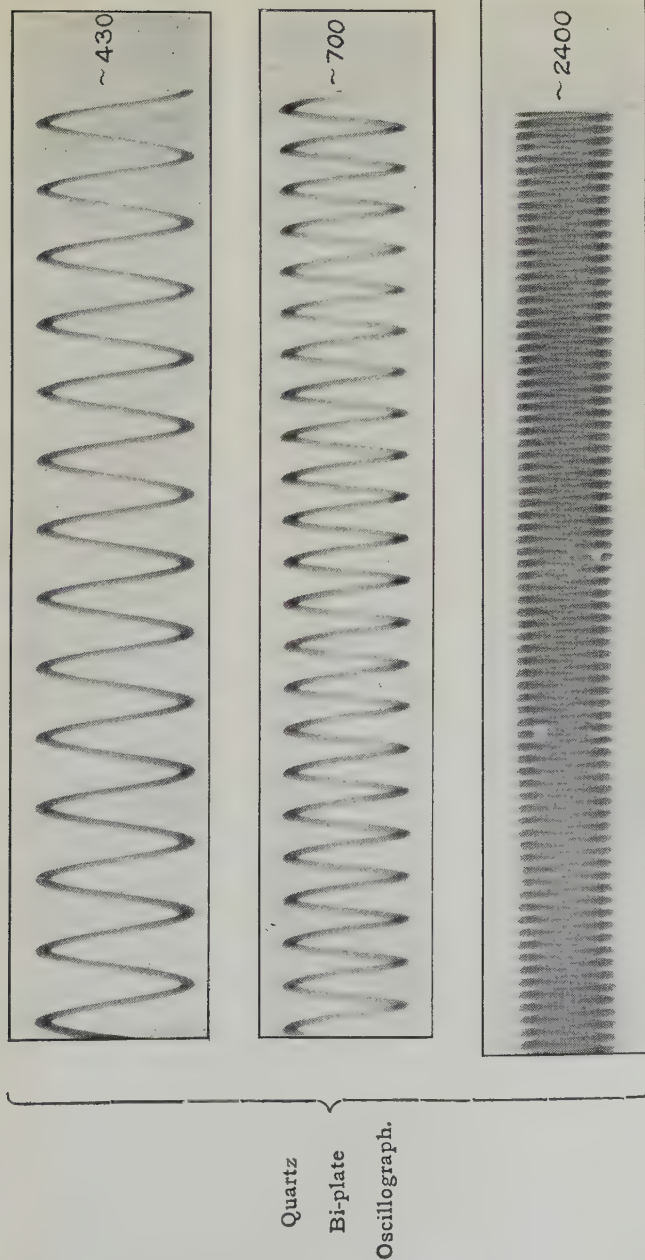
b. Double-Strip Quartz Oscillograph.



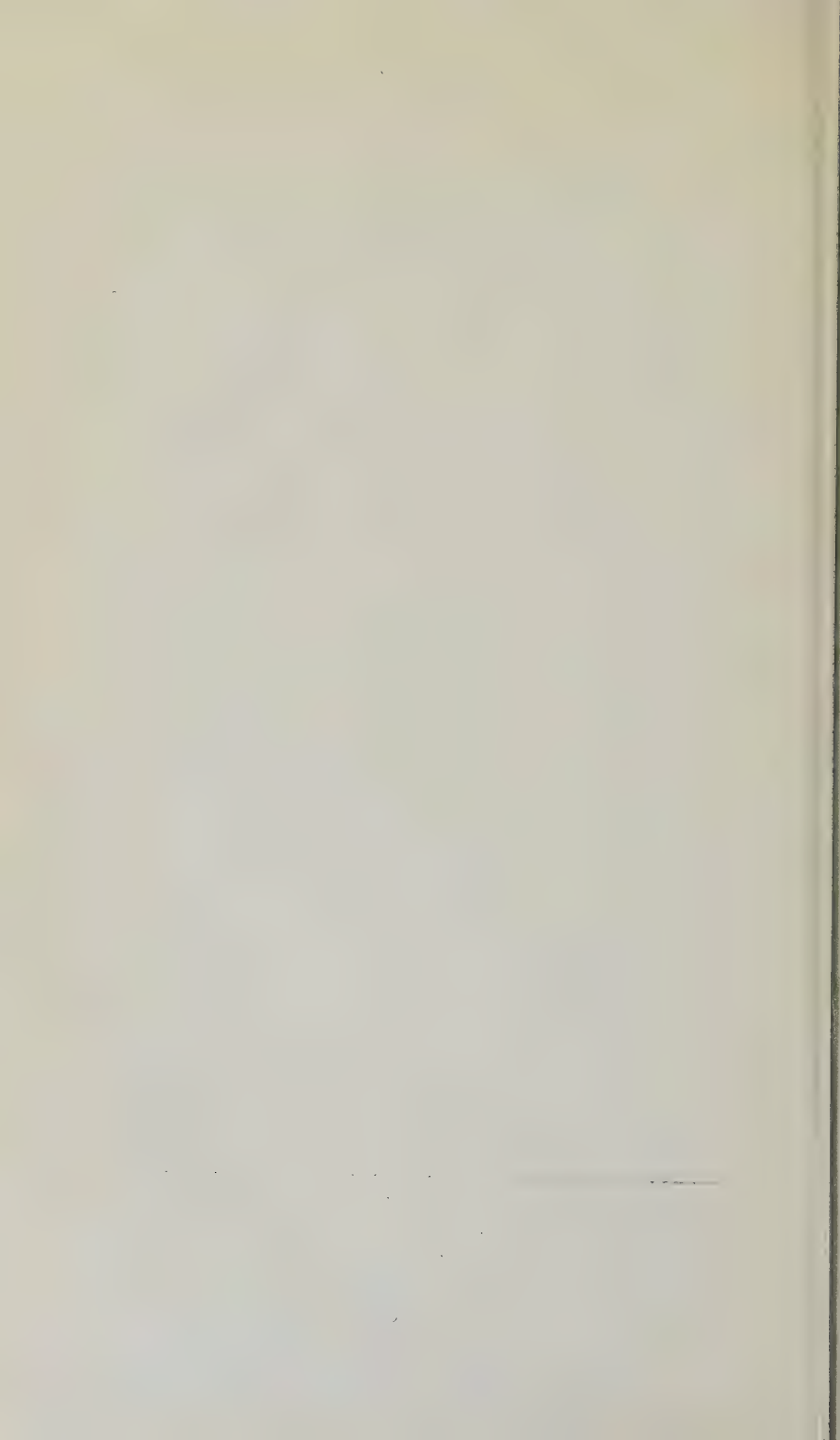
c. Single-Strip Rochelle Salt Oscillograph.

Fig. 4.





Piezo-Electric Oscillograph Records (using dropping-plate camera).



construct a double-strip rochelle-salt oscillograph. It is to be anticipated that this would be extremely sensitive even at high natural frequency.

A number of A.C. records obtained with the piezo-electric oscillographs are shown in fig. 4 (Pl. XXII.). (A dropping-plate camera was used.)

The excellent paper of Mr. Wynn-Williams and the oscillograph records obtained by him using rochelle salt serve without further remarks here to emphasize the advantages of the piezo-electric oscillograph. Of course there are certain obvious limitations as compared with other forms of electrostatic oscillograph, the sensitivity, for example, being considerably less than that of the E.S. string oscillograph. On the other hand, its simplicity and cheapness of production are points in its favour.

LXVII. *A Mathematical Statistical Investigation concerning Sub-electrons* *. By HERBERT DAECKE, Dr. rer. nat. of Hamburg †.

THE controversy concerning sub-electrons has by no means been definitely decided, either in favour of Ehrenhaft ‡ or of Millikan § in spite of the fact that this controversy has been of sixteen years' duration. The lack of agreement between Ehrenhaft and Millikan is indeed to-day partly removed by the fact that all physicists who have measured electrical charges of particles of a sufficiently small radius according to the method of Ehrenhaft have found charges that substantially fall short of the value $e = 4.77 \times 10^{-10}$ E.S.U. for the elementary quantum of electricity. The difference consists only in the fact that whereas the one group regards the sub-electrons as actual, the other believes that the shortage in value is only an apparent one produced by various causes. So many different things are indeed cited as causes, that it seems entirely out of the question to take up a clear and unique position on the matter. One physicist refuses to accept as an explanation the causes

* Cf. *Phys. Zeitschr.* xxv. pp. 624-631 (1924), and the detailed treatment in *Zeitschr. f. Phys.* xxxi. pp. 552-575 (1925).

† Communicated by the Author.

‡ F. Ehrenhaft, *Anz. Wiener Akademie*, March 4, 1909; April 21, 1910; May 12, 1910; *Wiener Ber.* cxix. p. 815 (1910); *Phys. Zeitschr.* xi. p. 940 (1910); *Ann. d. Phys.* xlv. p. 657 (1914); lvi. p. 1 (1918); lxiii. p. 773 (1920).

§ R. A. Millikan, *Phys. Zeitschr.* xi. p. 1097 (1910); *Phys. Rev.* xxxii. p. 349 (1911); *Phys. Zeitschr.* xiv. p. 736 (1913); *Phil. Mag.* xxxiv. p. 1 (1917).

cited by another, and indeed partly for good reasons. Some intimations are given in the following*.

O. W. Silvey †, working with Millikan, regards the particles which give charges smaller than e as impure mercury or as dust particles, and simply disregards them for subsequent computations. M. König ‡ and E. Radel §, following E. Regener ||, put the responsibility for the shortage in value upon the gas which is supposed to surround the particle in the layer of 10^{-6} – 10^{-5} cm. thickness. In a more recent paper of E. Wasser ¶, the proofs for this are made to appear unquestionably dubious. The hypothesis of Regener is likewise in other respects but weakly supported. This is shown not only by the decisive refutation on the part of a student of Ehrenhaft, Th. Sexl **, but also by the rejection of this assumption by R. Bär ††. Bär, however, also observed shortages. As K. Wolter ‡‡ had shown that these could not be explained by the invalidity of the Stokes-Cunningham law of resistance, Bär resorted for their explanation to the assumption of altered abnormally small densities. This assumption of Bär's has, however, met much the same fate as he himself imposed upon the hypothesis of Regener. F. Ehrenhaft §§ not only advances convincing opposing arguments, but L. Schiller ||| likewise finds densities of 0.2 for platinum, for example, highly improbable. Schiller believes the shortages in charge to be explained by departures from spherical form.

One contradiction is here seen to follow upon another. A fitting treatment hence seems to me to be one which, unburdened by prejudice, examines the entire complex of facts not by purely physical, but by mathematical statistical methods.

The observations applied for our investigations are those of M. König ¶¶ on mercury in air and carbon dioxide gas, and those of E. Radel *** on mercury in air. On arranging

* In more detail in the articles cited in the first footnote on p. 637.

† O. W. Silvey, *Phys. Rev.* vii. pp. 87–105 (1916). (Cf. also Y. Ishida, *Phys. Rev.* xxi. p. 561 (1923).)

‡ M. König, *Zeitschr. für Phys.* xi. pp. 253–259 (1922).

§ E. Radel, *Zeitschr. für Phys.* iii. pp. 63–88 (1920).

|| E. Regener, *Sitzungsber. d. Preuss. Akad.* (1920), pp. 632–641.

¶ E. Wasser, *Zeitschr. für Phys.* xxvii. pp. 226–236 (1924), in particular p. 231 et seq.

** Th. Sexl, *Zeitschr. für Phys.* xvi. p. 39 (1923).

†† R. Bär, *Ann. d. Phys.* lxvii. pp. 157–200 (1922).

‡‡ K. Wolter, *Zeitschr. für Phys.* vi. p. 339 (1921).

§§ F. Ehrenhaft, *Naturw.* x. p. 980 (1922).

||| L. Schiller, *Zeitschr. für Phys.* xiv. pp. 6–13 (1923).

¶¶ M. König, *l. c.*

*** E. Radel, *l. c.*

their observations in order of decreasing radius, these observers record a point under which the charge is *substantially* less than $e = 4.77 \times 10^{-10}$ E.S.U. (M. König gives the limiting radius 1.2×10^{-5} cm. for mercury in air, and 2×10^{-5} cm. for mercury in carbon dioxide gas; E. Radel the limiting radius 9×10^{-6} for mercury.) As my investigations are designed to make clear the relationships among the *sub-electrons*, I have applied this fact as a natural *basis of classification* for my statistics. The great significance of this step, which avoids using as statistical material those charges which lie close to 4.77×10^{-10} E.S.U. or multiples thereof, will be made clear on discussing the results obtained.

Of all the substances upon which observations of charge have been made with the Ehrenhaft condenser, mercury has been selected because a number of sources of error which are present for other substances disappear for mercury. Substantial shortages have not been established by all observers for oil and paraffin. Copper, sulphur, and selenium have firstly been comparatively little investigated, and secondly cannot lay the same claim to chemical definiteness and stability as can the noble metals*. Although it can hardly be expected that platinum, gold, and silver particles depart very strongly from spherical form, the sphericity of form of mercury particles is an indisputable fact†. Furthermore, mercury particles can, on account of their high coefficient of reflexion, be made visible in sizes in which particles of other substances (oil, glycerine, water) are completely imperceptible optically.

Let us now take from König's experiments those 24 values of the charge on mercury in air which substantially fall short of $e = 4.77 \times 10^{-10}$ E.S.U. We may then propose the following question:—*How great is the probability that these 24 values are integral multiples of a fundamental charge (e. g. of $0.50 \cdot 10^{-10}$ E.S.U.), this fact being concealed only by the error dispersion?* This question is similar to the more previous one which inquires into the hypothetical fundamental charge of which the observed charges are integral multiples. It can be answered very well by means of a criterion for integers that R. v. Mises‡ has set up by means of the cyclical theory of errors. He applied it at the time to atomic weights. If, namely, the 24 values of charge be plotted on a line which is then wound upon a circle of circumference 0.50, the criterion

* F. Ehrenhaft, *Sitzungsbr. d. Wiener Akad.* cxxiii. [2a], p. 62 (1914).

† Cf. F. Ehrenhaft, *l. c.* pp. 87–95 and Table III.; also E. Wasser, *Zeitschr. f. Phys.* xxvii. pp. 208–209, 211, figs. 1 & 2 (1924).

‡ R. v. Mises, *Phys. Zeitschr.* xix. pp. 490–500 (1918). Here is also given the exact meaning of the various quantities.

for integral multiples is given by the magnitude

$$K = 2\pi C(kn\alpha)e^{kn\alpha \cos \alpha}$$

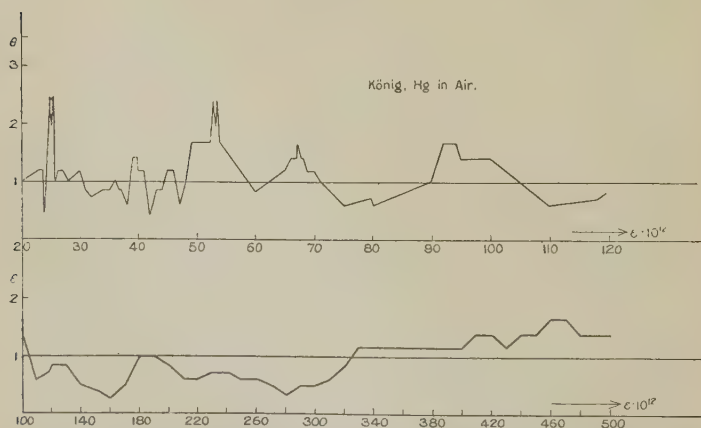
(n number of observations, a and α polar coordinates of the centre of mass of the statistical distribution, k coefficient of precision). The more K exceeds the value 1, the more plausible is the assumption that the values are integral multiples. If $K < 1$, this assumption is to be repudiated. If K is exactly equal to 1, either assumption is equally justifiable.

For our problem concerning sub-electrons, we propose the following more far-reaching question: *For what value of ϵ does K attain a relative maximum?* To answer this question it would be necessary to compute K for many values of ϵ . As this would require an immense amount of work, we introduce a quantity Q which seems to give an excellent preliminary orientation concerning the maxima of K :

$$Q = \frac{Z_1 + Z_4}{Z_2 + Z_3}.$$

(Z_i number of observations in the i th quadrant after winding upon the circle.) Q is seen to be easily computable. At those points at which Q is a maximum K is to be more exactly computed.

Fig. 1.



We must finally say something concerning the justification of applying the cyclical theory of errors to a definite group of observations. This is demonstrated by the agreement of the theoretical error integral with the summation corresponding to the actual error distribution, this summation being representable as a step-like curve.

Fig. 2.
König, Hg in Air.

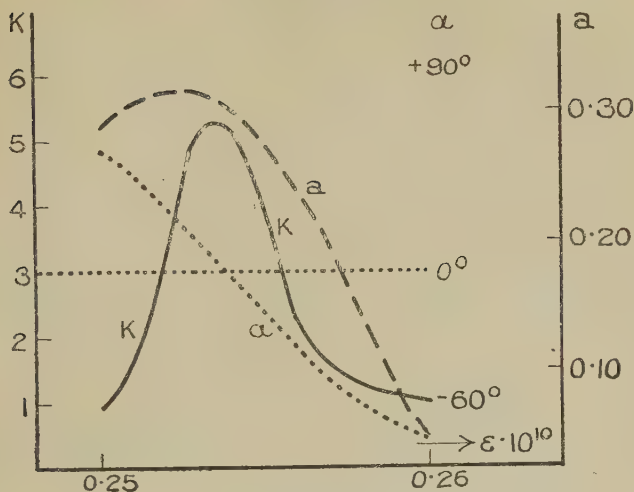
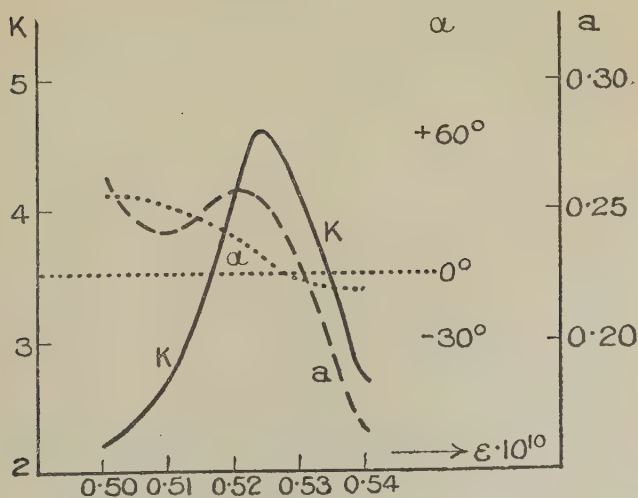


Fig. 3.
König, Hg in Air.



We give as an example the results for the observations of König on mercury in air. The Q -curve is shown in fig. 1. The maxima of Q are distinctly recognizable. The values of a , α , and K are more exactly computed for four points. (Figs. 2-5.)

Fig. 4.

König, Hg in Air.

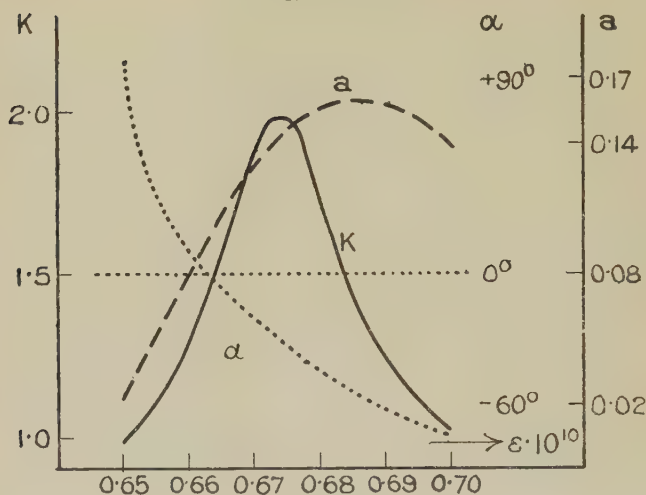
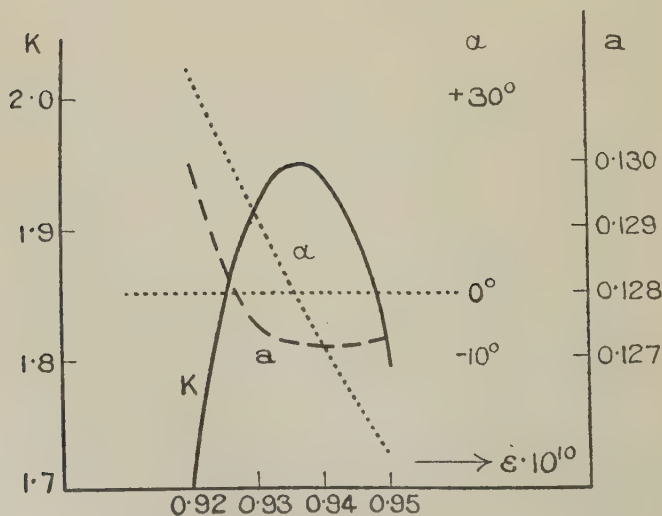


Fig. 5.

König, Hg in Air.



One immediately notices the following remarkable fact:—*The four values of ϵ for which K is a maximum very nearly coincide with numbers obtained by dividing the elementary quantum 4.77 by small integers, the deviation being well within the limits of the accuracy of observation.* The fact that these integers are small is to be emphasized. Compare Table I.

TABLE I.

Maximum for	K.	e/N .	% error.
$\epsilon=0.2534 \cdot 10^{-10}$	5.30	4.77 : 19 = 0.251	0.956
$\epsilon=0.5242$	4.61	4.77 : 9 = 0.53	1.094
$\epsilon=0.674$	1.97	4.77 : 7 = 0.6814	1.086
$\epsilon=0.937$	1.95	4.77 : 5 = 0.954	1.782

Even by means of the Q-curve (fig. 1) further maxima are noticeable at the points

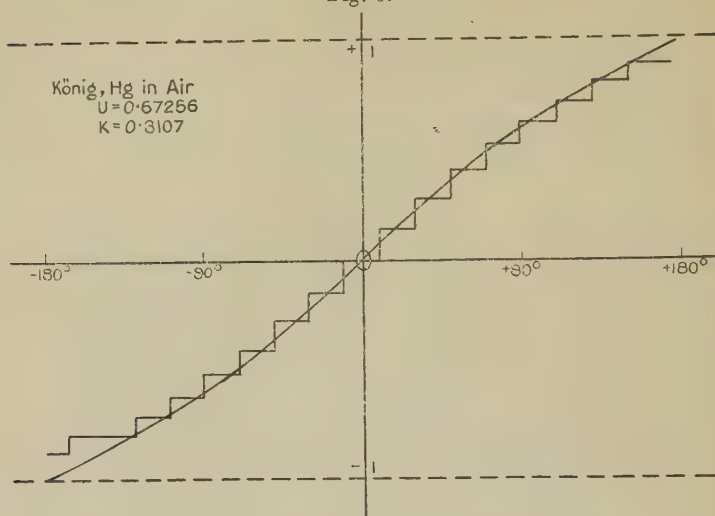
0.30	(corresponding to $0.2981 = \frac{e}{16}$)
0.36	(„ „ $0.3669 = \frac{e}{13}$)
0.3975	(„ „ $0.3975 = \frac{e}{12}$)
0.45–0.46	(„ „ $0.4542 = \frac{2e}{21}$)
0.79–0.795	(„ „ $0.795 = \frac{e}{6}$)
1.20–1.30	(„ „ $1.1925 = \frac{e}{4}$)
1.80–1.90	(„ „ $1.908 = \frac{2e}{5}$)
2.30–2.40	(„ „ $2.385 = \frac{e}{2}$)

For an exhaustive discussion of the foregoing as well as for the *confirmation by means of the linear theory of errors* of the remarkable conformity to order, reference may be made to *Zeitschr. f. Phys.* xxxi. pp. 564–567 (1925).

Fig. 6 illustrates the brilliant agreement between theoretical and experimental integrals of error.

That this conformity does not result from the particular chance circumstances surrounding König's arrangements for his experiments, but that it possesses objective value, follows from the fact that the same results appear not only for König's observations on mercury in CO_2 , but also for the entirely independent experiments of Radcl.

Fig. 6.



Summary of the results.—The assumption that the sub-electrons may be represented in the form $\frac{m}{n}e$, where n is not large and $m < n$, possesses greater probability than any other assumption.

Conclusions may be drawn in either of two directions. If the observations of shortages of the elementary quantum of electricity are to be reconciled with the proof for the existence of such a quantum, then it must be possible in some manner to refer these shortages to $4.77 \cdot 10^{-10}$ E.S.U. The fact that the apparently irregular shortages stand in the above mentioned relationship to $4.77 \cdot 10^{-10}$ E.S.U. can perhaps be useful in this connexion.

Another conclusion, however, is forced upon us as being at least equally probable: namely, that for small radii a division of the electron actually occurs, and in n parts. Of these n parts, m ($< n$) can occur as united*.

I have to thank Dr. phil. Frederick Doermann of Washington for his great kindness and trouble in translating this article from German into English.

Hamburg 23, May 11th.

* F. Ehrenhaft expressed this supposition as early as 1913; cf. F. Ehrenhaft, *Verhandl. d. Deutschen Phys. Ges.* xv. p. 1201 (1913), and his remarks in discussion of my paper at Innsbruck, *Phys. Zeitschr.* xxv. pp. 629-'30 (1924).

LXVIII. *Absorption of Light by Vapours of Pb, Sn, Bi, Sb, and Mg.* By Prof. A. L. NARAYAN, D.Sc., F.Inst.P., and K. R. RAO, M.A., Madras University Research Scholar*.

[Plate XXIII.]

Abstract.

ABSORPTION of light by non-luminous vapours of Pb, Sn, Bi, Sb, and Mg has been studied, and it has been found that the absorption spectrum of lead shows, besides the fundamental line λ 2833, a banded spectrum at about 1100° C., degraded towards the red and spaced at intervals of 32 \AA.U. nearly. Absorption spectrum of tin showed only a faint reversal of λ 2706.6. That of bismuth showed, besides λ 3067, 2524, 2276, and 2230 & 28, a typical banded spectrum containing about 20 bands. The absorption at each of these bands is very diffuse and complex, consisting of a number of finer bands. With increase of vapour density all these bands gradually fuse together (beginning from the short wavelength side) to form a region of continuous absorption. At about 1200° C. another typical banded spectrum appeared in the visible region extending from λ 6500 to λ 4500. The absorption spectrum of antimony showed fine lines at 2312 and 2306 and a banded spectrum extending from λ 2305 to λ 2250, while at higher temperatures there was another banded spectrum in the region 2830-3000 and a fine line at λ 2770. The existence of the banded spectra in the case of these metals of the higher groups of the periodic table leads us to the conclusion that the molecules of these elements are polyatomic. λ 4571, the single line spectrum of magnesium, has been for the first time photographed as an absorption-line by using a long column of the vapour.

DURING the past few months the authors have continued their studies on the absorption of light by vapours of different metals. It is the purpose of the present paper to give an account of the absorption spectra of Pb, Sn, Bi, Sb, and Mg.

No line series have been found in the spectra of the metals of IVth and Vth groups of the periodic table, nor is there anything known of the lines appearing at low voltages, as it is found very difficult to determine directly the critical potentials of such highly refractory elements. McLennan† has investigated the absorption spectrum of Pb and found that there was well-marked absorption at λ 2833 and λ 2170, and

* Communicated by Prof. A. W. Porter, F.R.S.

† McLennan and Zumstein: Roy. Soc. Canada, Trans. xiv. Ser. 3, Sect. 3, pp. 9-17 of 1921.

that no absorption was indicated at 10291 as shown by the resonance potential of the elements. Foote and Mohler* have pointed out that an isolated group of infra-red lines observed by Randall by thermopile measurements falls within this region. J. J. Dobbie and J. J. Fox† have studied the absorption of light by vapours of As, P, Bi, and several other metals up to 3100, and found there were no traces of any kind of selective absorption in the case of As, P, and Bi. Recently Grotrian‡ has published an account of his experiments on the absorption of light by vapours of these and some other metals. In all these experiments, the investigators used an absorbing column of metallic vapour maintained in a quartz tube heated electrically by a coil of nichrome ribbon. In the present experiments the authors used a charcoal furnace through which a powerful blast of air was maintained, to avoid any possible magnetic effect on the absorption lines, and the metal was enclosed in vacuum in an iron tube furnished with quartz windows. The absorption tube is exactly similar to the one used by the authors § previously and in their experiments on Thallium Vapour.

In all these experiments Kahlbaum's pure metals were used.

Fig. 1 represents the absorption spectrum of Pb at 1100° C.

Fig. 2 " " " " Bi; *a, b, c, d* being the photographs taken at gradually increasing vapour densities, *d* being the photograph at 1250 showing the banded spectrum in the visible region (Pl. XXIII.).

The absorption spectrum of Sb at 1150° C. has also been obtained. Owing to the low intensity of the carbon arc in this region, a good negative cannot be obtained.

The absorption of $1S-2p_2$, the single line spectrum of magnesium, has been obtained, but the photograph will not stand reproduction.

LEAD.

The absorption spectrum of lead shows the asymmetrical nature of the fundamental line, λ 2833 being sharply defined on the short wave-length side, and with increase of temperature gradually spreads towards the other end. This line

* 'Origin of Spectra,' p. 65.

† Roy. Soc., Proc. xviii. pp. 147-153, Nov. 3, 1920.

‡ *Zeits. f. Physik*, xviii. 3-4, pp. 169-182 (1923).

§ Phil. Mag. May 1923; and "Absorption of Lithium Vapour," Proc. Roy. Soc., Sec. A, July 1924, and "Absorption and Dispersion of Tl Vapour," recently communicated to the Royal Society of London.

obviously corresponds to the normal state of the atom and is probably the first of the series.

At about 1100° C. the vapour shows a faint banded spectrum, which has not been described previously, extending from 3100 to 3400. At still higher temperatures these bands become stronger and wider. The approximate wavelengths of the band heads are as follows :—

3352.3 Å.U.	3230.2 Å.U.
3321.5 „	3204.1 „
3290.0 „	3175.0 „
3260.0 „	3140.3 „

By using spark under water between two copper electrodes as the source of light, the authors found the vapour absorbed 2577, 2613, and 2614. Owing to the very low intensity of these absorption lines, these could not be successfully reproduced in the positives.

TIN.

The absorption spectrum of this element showed a faint reversal of the line λ 2706.6. No absorption was obtained at λ 3009.2 and λ 2863.4 as indicated by Grotrian, probably due to the fact that sufficiently high temperatures could not be obtained.

BISMUTH.

The spectrum of this element shows besides the "raie ultime" λ 3067 a typical banded spectrum extending from λ 2600 to λ 2900 Å.U. This banded spectrum is degraded towards the red and is spaced at intervals of about 15 Å.U. We have succeeded in photographing 20 of these bands. The absorption at each of these bands is very diffuse and complex, consisting of a number of finer bands. With increase of vapour density all these bands gradually fuse together (beginning from the short wave-length side) to form a region of continuous absorption. To find if there are any absorption lines in the region covered by the banded spectrum, photographs were taken at gradually increasing densities. A careful examination of the absorption spectrum at about 800° C. shows that at 2721.5, 2730, and 2745 there are fine absorption lines probably not in any way connected

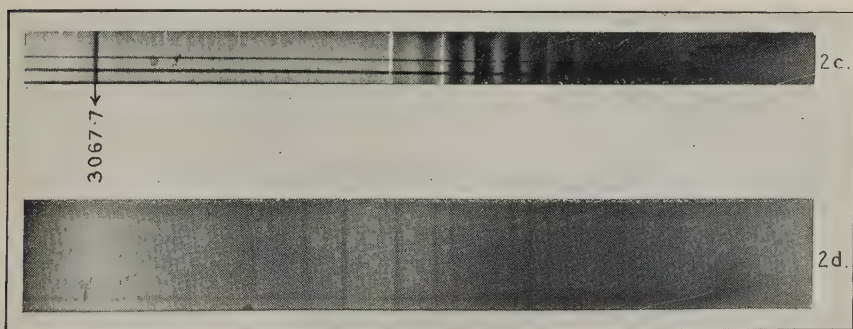
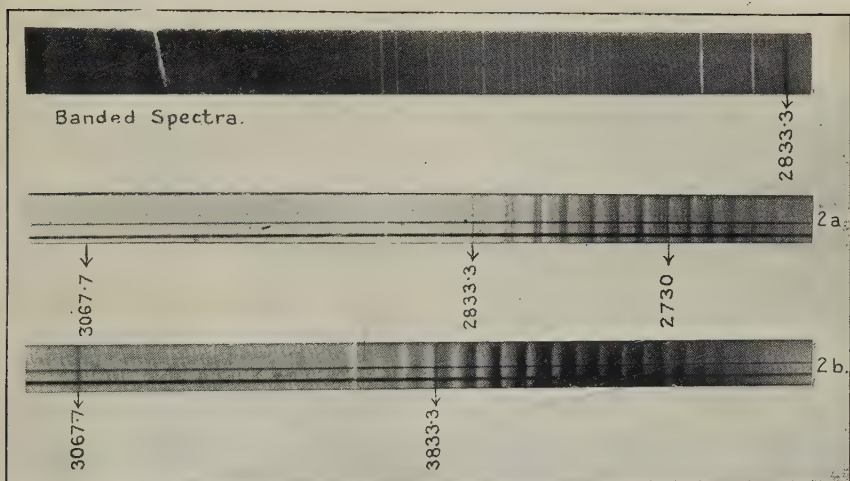
with the banded spectrum. With the dispersion available, though the wave-lengths of the fine lines composing the bands could not be accurately measured, the approximate wave-lengths of the band heads have been determined and are as follows :—

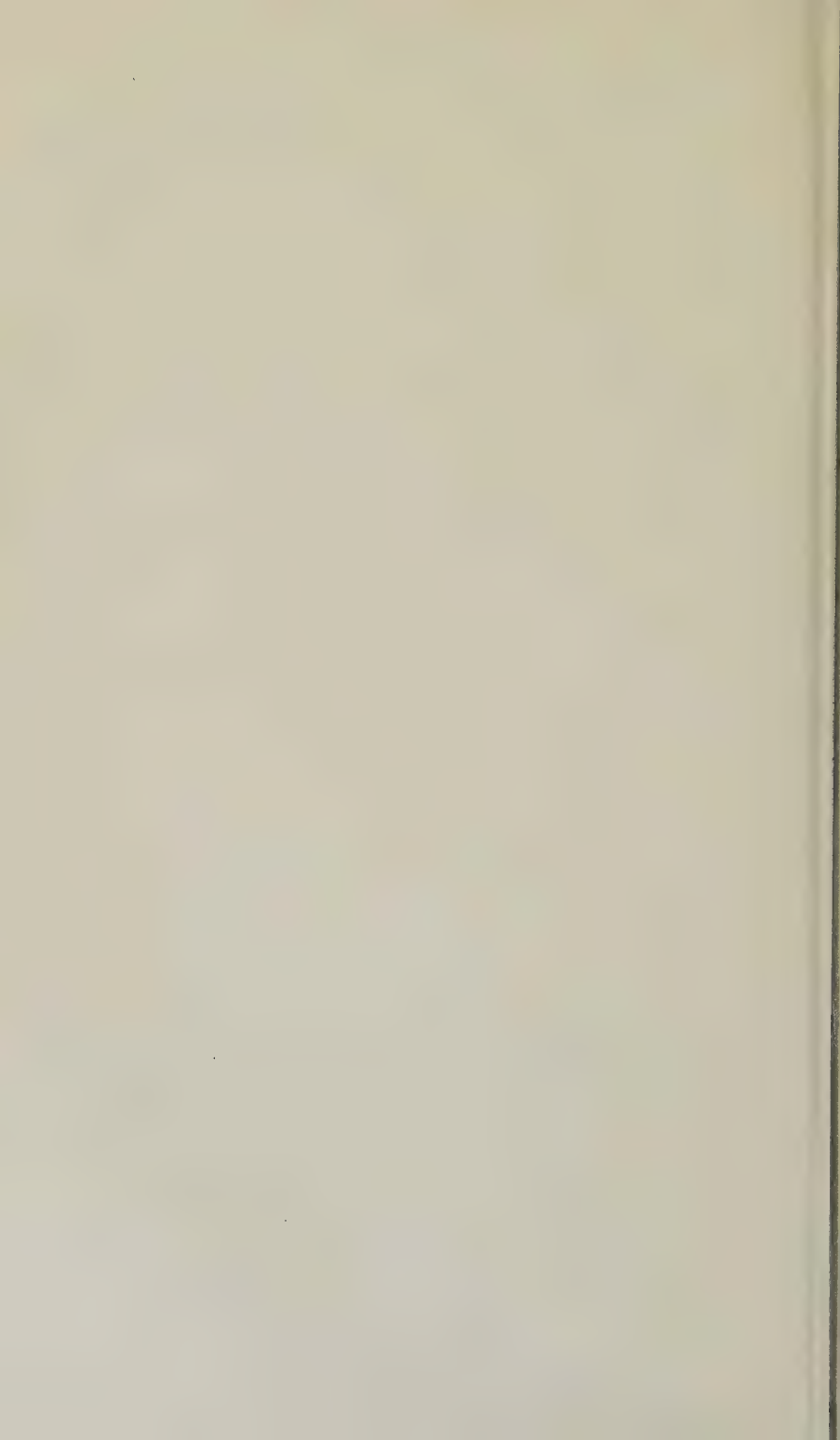
2855.9 Å.U.	2744.8 Å.U.
2842.9 „	2732.6 „
2828.2 „	2722.0 „
2813.5 „	2712.3 „
2799.8 „	2701.9 „
2785.0 „	2693.2 „
2772.7 „	2681.5 „
2759.6 „	2670.0 „

At about 1200° C. another typical banded spectrum appeared in the visible region extending from about λ 6500 to λ 4500. The interval between the band heads varies approximately from 90 Å.U. to 35 Å.U. as we go from the red end to the violet end. These bands show a distinctly fine structure. These bands also become stronger and wider with increase of temperature. But temperatures sufficiently high to develop these bands could not be obtained. Fig. 2*d* shows the banded spectrum in the visible region at about 1250° C. At this temperature the transmitted light was light violet in colour. By using spark under water between two stout copper electrodes as the source of light, the authors found that at 900° C. the vapour absorbed 2524, 2276, 2230, and 2228.

ANTIMONY.

The absorption spectrum of this element shows fine lines at λ 2312 and λ 2306 and a banded spectrum on the short wave-length side of these lines extending from 2305 to 2250 with a constant interval of 15 Å.U. nearly. The line λ 2312 is probably the same as λ 2313 noticed by Liveing and Dewar as a reversal line in the arc. At higher temperatures continuous absorption begins from the short wave-length side and extends into this region. As the temperature was raised still further the absorption spectrum





showed another banded spectrum in the region λ 2830 \rightarrow 3000 and a fine line at λ 2770.

The existence of the banded spectra in the case of these metals of the higher groups of the periodic table leads us to the conclusion that the molecules of these elements are polyatomic.

MAGNESIUM.

The absorption spectrum of this element at high temperatures clearly shows λ 4571, $1S-2p_2$, the single line spectrum of the element which McLennan * was not able to observe. But the fact remains that this line appeared only at high temperatures, although one would expect from the quantum theory that this single line spectrum of the element should be first absorbed by the non-luminous vapour of the metal.

Our thanks are due to Messrs. G. Subrahmanyam and D. Gunniah, of the Department, for the assistance they have given in taking the photographs.

Research Laboratories,
H.H. The Maharajah's College,
Vizianagrum.

Note added in Proof, June 20th.—Since these results were communicated, further experiments have been conducted in this laboratory on “Fluorescence and Channelled Absorption of Bi Vapour,” the results of which were published in a recent number of the Royal Society. Prof. McLennan and his collaborators have recently studied the arc reversals of Pb and Sn with a fluorite spectrograph (Roy. Soc. Canada, Trans. xviii. Sect. 3, 1924, pp. 57–75 & 77–78).

* Roy. Soc. Proc. vol. xcii. p. 574 (1916).

Absorption of this line, 4571, was consistently observed by the authors in their experiments on magnesium vapour, and the fact was communicated to the Astrophysical Journal, in a short note, on account of the considerable interest that centres round this line. But we have now succeeded in photographing this line, and therefore this portion also is included in this paper.

LXIX. *The General Nature of Band Spectra.* By J. W. NICHOLSON, M.A., D.Sc., F.R.S., Fellow of Balliol College, Oxford*.

THE present paper proposes to suggest, in an introductory manner, the mathematical relation between band and line spectra. Following on the investigation of Curtis †, the theory of band spectra has recently received much development, and their origin, in the light of the quantum theory, is at least partially understood. Investigations have so far been restricted to an analysis of the spectral effect of the rotations of the molecule as a whole, constituting a special case of the quantization of the motions of a system containing more than one nucleus, but a case worked out in strict accordance with the opinion, now generally held, that a band spectrum can only arise from a system of a non-atomic, or at least doubly-nuclear structure. In a later paper, the analytical treatment, at least in an approximate manner, of the motions in a molecule which are consistent with less special motions of the nuclei, will be developed, with the type of spectral formula for bands to which it leads. At present we confine attention to a general account of a formula which appears to be capable of supplying the link between band and line spectra, with the consequent suggestion of the meaning of the appearance of Rydberg's constant in the former—as in Fowler's investigation of the band spectrum of Helium, where alone it has appeared hitherto in the precise manner of series spectra—and the manner in which its mode of occurrence may be looked for.

We must, in the first instance, review the main properties of band spectra in their many ramifications of type, as deduced entirely from the experimental side, with suggestions, at various points, as to the probable theoretical significance, on the lines of the quantum theory, of the complex phenomena which they present. Deslandres, to whom so much of the empirical work on band spectra is due, would apparently still regard a band spectrum as a possible emission from atoms, but if we accept the principles of the quantum theory of emission in their entirety, this possibility disappears—as can, in fact, readily be shown analytically—and we are compelled to regard even the band spectrum of Helium as due to a temporary molecular association of Helium with itself, or Hydrogen, which exists under the conditions effective in a vacuum tube during the passage of a discharge.

* Communicated by the Author.

† Proc. Roy. Soc. A, ciii. (1923).

Band spectra appear most usually when the source is only feebly excited, and tend to disappear with a further excitation strong enough to develop the line spectra, although there are certain exceptions, as, for example, the band spectrum of Helium, and at least certain portions of the secondary spectrum of Hydrogen which are probably of a banded type—the “lines” not showing a normal Zeeman effect. In a case like Helium, where any excitation at all is necessary to form temporary molecular aggregates which can exist for a sufficient time during the discharge to develop a characteristic spectrum, it may well occur that a stronger excitation may be capable of developing and maintaining more complex aggregates, with a consequent actual increase in the intensity of some of the bands from such sources. Hydrogen, again, is known to form the aggregate H_3 molecule, but under conditions not very clearly defined. It is possible that this and others require a specific degree of excitation and consequent ionization for their optimum production. Many of the extremely weak lines in the secondary Hydrogen spectrum may proceed from such origins of a temporary kind.

Deslandres, in 1887, proposed that all band spectra should be represented by the very general formula

$$n = f(m^2 p^2) s^2 + B m^2 + \phi(p^2),$$

where n is the wave-number of the line in a band, (m, s, p) are integers, and f, ϕ quite arbitrary functions, but B constant throughout the band. At the same time, (f, ϕ), though arbitrary, were expected to be comparatively simple functions. Generally speaking, after the manner of use of this formula, it might be said that a band spectrum was viewed as a network of lines whose wave-number intervals formed three sets of arithmetic progressions, determined, at least approximately, by three integers. In other words, it was presumed that f and ϕ were effectively quadratic functions only, in m or p . A consequence is that the spectrum can usually be subdivided into sets of lines following formulæ of the simple type

$$n = A \pm B m^2,$$

though it is now more usual to require the type

$$n = A \pm B m \pm C m^2.$$

Deslandres subsequently put forward the simpler formula

$$n = A + B(m + \alpha)^2 - C(r + \beta)^2,$$

where m and r are integers, as representing the positions of

the "heads" of a complete band, where B and C are both necessarily positive.

As regards the general effectiveness of this formula, the following classical instances will suffice :—

(1) The "Swan" spectrum of Carbon is given by

$$n = 11.64(m + 0.83)^2 - 19.60(r + 0.03)^2 + 2407,$$

where m ranges from 63 to 69, both inclusive, and r from 45 to 53 inclusive.

(2) The first group of Cyanogen bands satisfies :

$$n = 12.90(m + 0.6)^2 - 8.60(r + 0.8)^2 - 974,$$

with m ranging from 73 to 79 and r from 56 to 66.

(3) The first group in the spectrum of Nitrogen is given by

$$n = 22785.1 + 14.6815(m + 0.5)^2 - 15.1595r^2,$$

with m ranging from 34 to 48 and r from 37 to 53.

The first formula is due to Jones and Watts, the second to Fowler and Shaw, and the third to Deslandres.

The actual number of band spectra which have been thus represented by three parameters is about 17. It is of interest to note the number of individual band-components thus taken account of, which in the preceding cases is as follows :—

Case 1, 63 ; Case 2, 77 ; Case 3, 255.

So that it is quite clear that this simple Deslandres's formula is very frequently a close approximation to the actual laws.

The first comment which the quantum view of spectra must suggest relates evidently to the large values of the integers concerned. On this view, an integer occurring in a spectral formula means, of necessity, that some possible motion of a system, or a part of it, has been quantized, and that if the motion can be defined by a generalized coordinate q , the phase integral of the momentum with respect to q is the product of Planck's constant h and the integer concerned. We are not, at this point, necessarily supposing that the motion is of the type ordinarily called "pseudo-periodic," in that the coordinate q repeats itself in a specific period with no necessary relation to the periods of repetition of other coordinates which, in the Lagrangian sense, are formally independent of q in an analytical manner. Yet, of course, it may be contended that the analytical formulation

$$\oint p dq = nh$$

is, at present, our only basis for the introduction of integers by the quantum theory, and that all spectra which are functions of integers necessarily proceed from pseudo-periodic motions to which this mode of formulation can alone apply—even if, by our failure to separate the variables in Jacobi's sense, such motions cannot be found, or even shown to exist, except in the simplest cases. The existence, as shown by the late Sir George Darwin and others, of the so-called "periodic orbits" in cases of the problem of three bodies as it occurs in astronomy, with variables completely unseparable by any known analytical method, is, in our view, a sufficient indication that such orbits must be presumed to exist in any problem of a set of moving gravitational masses (or electrical charges, such as nuclei and electrons) which can retain a configuration appropriate for a continued existence in the form of the "steady states" necessary for a consideration, by the quantum theory, of emission spectra, and that such states are required by the mere existence of such spectra.

Certain suggestions towards the generalization of the phase-integral specification have occasionally been put forward, but, if the preceding argument be granted, it would seem that there is no necessary generalization, but only the recognition that pseudo-periodic motions exist even if they cannot be determined exactly, and that any radiating atom or molecule is necessarily passing between two such states, which are the only possible configurations for an atom or molecule not temporarily subject to radiation or absorption of energy. We are implying, in other words, that the formulation

$$\oint p dq = nh,$$

which, in the hands of W. Wilson, Sommerfeld, and others, has been completely effective in interpreting extreme detail in all cases where Jacobi's analytical method is applicable, remains the final generalization which regulates the dynamics of the atom or molecule, and that, for example, if we could find a suitable analytical procedure, it would be equally effective in giving a strict numerical interpretation of the arc spectrum of Helium.

The large integers involved in the representation of band spectra, according to this view, presuppose motions in the emitting system which involve enormous multiples of h in their phase integrals. We only need to consider the simple

hydrogen atom in order to show that they cannot be motions which appreciably depend on the outer electrons.

Any system containing an electron on its outer "rim," if that electron participates essentially in a motion of quantum number 50, must have a general "radius" comparable with 2500 times that of a Hydrogen atom—which is a quite impossible value. If τ is the quantum number and m the moving mass, the radius is of order determined by $\frac{\tau^2}{m}$. If,

however, the moving mass is a nucleus, of mass comparable with M , that of a Hydrogen atom, this is at once reduced to a relative order

$$\tau^2/1830m,$$

and a number like $\tau=50$ has no effect on the order of magnitude of the distance between nuclei in a molecule, and consequently does not affect the order of magnitude of the molecular radius.

The conclusion is almost irresistible that such large integers constitute an effective proof that the motions of nuclei in molecules are to be quantized like those of electrons, and that such a procedure does not violate the restrictions to the radius of emitting systems which are imposed by other physical considerations.

Moreover, while, on the quantum theory, there is a severe limitation to the possible integers, dependent on the pressure of a gas, in its atomic state emitting a line spectrum, no such restriction operates in the case of a band spectrum. It is clearly possible, in a quantitative manner, for even a thousand members of a band to be shown without any interference with the size of the molecule which the pressure imposes.

Such a supposition is, of course, inherent in the work which has been done on band spectra arising solely from rotations of a molecule as a whole. The preceding argument shows that it is quite general when the nuclei are allowed to move in any manner consistent with the pseudo-periodic type of motion and the quantizing principle in its ordinary form.

If band spectra are subject to the quantization of nuclei, it follows that no band spectrum contains any new absolute constant of nature not already inherent in line spectra. Apart from the fine structure of the latter, determined solely by the relativity correction for a moving mass, this implies that the universal constant of bands is still that of Rydberg only, though, at present, it has only been demonstrated in the case of Helium.

The only writer who, till recently, attempted to obtain a universal form of relation between band and line spectra was Halm*, who gave, on purely empirical grounds, a formula of some significance, capable of including, on the one hand, line spectra and, on the other, band spectra, as limiting cases. Its significance, at the time of its development, really lay in the fact that it provided bands with a "tail" as well as a head—a phenomenon which actually occurs in certain cases. Further knowledge of band spectra has not confirmed the *type* of formula suggested by Halm, but his investigation is still classical as the first definite essay towards a relation between spectra of the two forms. Recent knowledge has only served to enhance the fundamental importance of a somewhat neglected memoir.

We have already said that the first connexion between line and band spectra, in an ultimate sense which brings theory into play—though itself founded on a purely experimental study,—was due to Fowler in 1915. Fowler showed† that in the special case of Helium bands (now believed generally to be due to a temporary Helium compound or molecule), the "heads" satisfied a formula of the Rydberg type—not very accurately, but effectively if the Ritz or Hicks modifications of Rydberg's formula were used. These heads are doublets, and Nicholson‡ showed later that the separations in wave number of these doublets vanished at the limit of the series, so that the series obtained by Fowler were "Principal Series" in the strict sense of line spectra. Although the details of the bands have been discussed further by Curtis, it is not yet possible, on the basis of this spectrum alone, to develop a composite formula which shall exhibit the whole band spectrum in a formula of the type Halm attempted to obtain, which will indicate the precise nature, from the point of view of atomic theory, of the constants involved.

But we may argue from the Helium band spectrum, which in many respects is quite a typical one, to other band spectra, and we may conclude with some certainty that the Rydberg constant is, in fact, present in all band as well as line spectra, though not necessarily in the simple and strictly analogous manner in which it occurs in line spectra. We may, indeed, go further, and say that if the "heads" of the bands—not always directly visible as strong parts of the bands, and often only calculable when the appropriate

* Trans. Roy. Soc. Edin. 1895.

† Proc. Roy. Soc. A, xci. (1915).

‡ Proc. Roy. Soc. A, xci. (1915).

mathematical representation of the band has been previously elucidated—were known, they might be expected always to obey a Rydberg type of formula suitable for the heads as members of a line spectrum. Uniformity in physical phenomena would alone preclude any uniqueness regarding the heads of such a typical band spectrum as that of Helium.

Since the constant in the series formula for the Helium band heads is N , that of Rydberg, the principles of the quantum theory compel us to suppose that, whatever be the emitting system, it is one in which one electron is more remote than all the others. It would, therefore, be expected that this spectrum should be subject to the Zeeman effect—a matter in urgent need of test. For such a test would be a strong confirmation of the essential correctness of the quantum theory even in its predictions of the existence of “ $4N$ ” and “ $9N$ ” series in atomic systems which have lost two or three electrons respectively while one is returning. If molecular structures, as we may expect, are capable of similar losses, it is necessary for the returning electron to be very remote compared with others—the molecule thus behaving roughly towards this electron as a charged atom might do,—in order that a whole number multiple of Rydberg’s constant should determine the spectrum as an external multiplier.

Otherwise, if the electrons all remain at similar distances from the nuclei in the initial and final stationary states, no such simple multiple can be expected. As an illustration, it is sufficient to consider an *atom* with a single nucleus *ve* and n electrons *in a ring*, which passes to another ring.

The spectrum, in wave number, is

$$n = N(\nu - \frac{1}{4}S_n)^2 \left\{ \frac{1}{\tau_1^2} - \frac{1}{\tau_2^2} \right\},$$

where τ_1 and τ_2 are integers, and the multiplying constant is, not Rydberg’s N , but

$$N(\nu - \frac{1}{4}S_n)^2,$$

which may be an incommensurable multiple. S_n , of course, is here the usual

$$S_n = \sum_{s=1}^{n-1} \operatorname{cosec} S\pi/n.$$

Such incommensurable multiples are clearly to be expected in the usual band spectra, if due to molecules, for such molecules must contain many transitions between states in which—for both original and final states—no electron is less intimately associated with the nuclei than any other. In our

view, it is almost probable that the search for Rydberg's constant in band spectra, except in peculiarly special cases, like that of Helium where it occurs without such a multiplier, has failed for this reason. But it would seem clear that the heads of bands in any such spectrum, if they are really the true "heads"—a matter sometimes in doubt,—should always follow a Rydberg type of formula,

$$n = N\alpha \left\{ \frac{1}{(\tau_1 + \mu_1)^2} - \frac{1}{(\tau_2 + \mu_2)^2} \right\},$$

where τ_1 and τ_2 are integers, and α is a purely numerical constant with a significance like that of $(\nu - \frac{1}{4}S_n)^2$ in the preceding discussion of atoms.

It is, perhaps, only necessary to add that, even for the purpose of preserving N as the constant of the ordinary arc spectrum of Helium, we have to suppose that, of the orbits of the two electrons in the neutral state, one is very much larger than the other.

We conclude, therefore, that incommensurable multiples of the Rydberg constant may be the prevailing factors in the majority of band spectra, and if these factors are elucidated and identified in simple cases, such as the band spectrum of Hydrogen, they give valuable knowledge in themselves as to the nature of the molecular configuration. Moreover, an ordinary Zeeman effect should only be expected when the constant is N itself.

We now return to the more descriptive portion of some of the phenomena characteristic of band spectra. The large integers are quite general, and it is rarely that any integer less than 30 is found. Deslandres, in fact, considers that the bands corresponding to small integers are usually in the unexplored part of the infra-red region.

If, to the preceding formula, we add a term to take account of the "degraded" part of the band, towards red or violet, the complete formula becomes

$$n = \pm A + B(m + \alpha)^2 - C(r + \beta)^2 \pm (s + \gamma)^2 f(m^2, r^2),$$

where all the coefficients are positive in known bands, and (m, r, s) are three integers. The coefficient $f(m^2, r^2)$ varies from one band to another, and is invariably very small, at least 50 to 200 times smaller than B or C .

Sometimes the term with B is absent, and sometimes that with C . For example, in the absorption spectrum of Oxygen,

there are 5 bands, whose representative formula may be written as

$$n = 48788.8 - 14.112(r + 0.2775)^2$$

$$(r = 46, 47, \dots, 50),$$

without the additive term, and, on the other hand, Fowler has shown that the so-called "Fourth group of Nitrogen bands" has no coefficient C , but only the additive term. Moreover, only two or three values of one of the integers may appear.

The carbon monoxide spectrum, as shown in comets, for example, gives bands corresponding to seven values of r , but only two values of m . Instances of the converse, if less frequent, are nevertheless available, and there is no real distinction, on this basis, between the integers m and r in the nature of their occurrence in spectra.

Now the absence of any particular integer, or its mere restriction, for purposes of visual spectra, to a very limited number of consecutive values, should, on the general view we are developing in accord with the quantum theory of spectra, indicate only that the effective degrees of freedom of the stationary states of the molecule, associated with the bands, are restricted—perhaps by the physical conditions which prevail. This can easily be seen if we consider that such states must fall into distinct *types*, in which, on passing from one state to another—both being defined, as indicated previously, by pseudo-periodic motions,—no motion, or change of motion, takes place in certain coordinates, and no corresponding quantum numbers can therefore appear in the formula for the bands. Such motions are, in fact, so infrequent that at any time there cannot exist a number of molecules, in the region examined, effective for the production of a radiation capable of affecting a photographic plate. For example, if a molecule contains only two nuclei, sets of stationary states must ordinarily exist in which the arrangement continues to be symmetrical about the line joining the nuclei—as, in fact, in the purely rotational band spectra hitherto discussed,—and, in this eventuality, passage from one state to another only involves motion of nuclei along the line joining them, and not in their other degrees of freedom.

This is, of course, equivalent to a statement that such incomplete band spectra result from passages between molecular stationary states which belong to the "degenerate cases" of the general orbits, which are theoretically possible

for a molecule under the fundamental quantum principle—which we consider to be the essential formulation,—that

$$\oint p dq = nh$$

for every degree of freedom of every electrical charge, *positive or negative*, in the molecule.

Again returning to the general descriptive formula of band spectra, we note that the functions $f(m^2, p^2)$ are very frequently constant—within the limits of experimental error,—especially if the starting-points of the integers m and r , which are never, by experiment, entirely determinate, are chosen suitably. This has been shown clearly by a somewhat fundamental investigation of Heurlinger*. We could, however, refer back even so far as to Moseley's classical investigation of the X-ray spectra of the elements, where an exactly similar mathematical difficulty appears. The leading lines of these spectra had wave numbers proportional to $(N-\alpha)^2$, where N increases from element to element by unit steps, and α is an incommensurable, and not small, magnitude. The *absolute* value of N cannot be determined by any experiment, and it remains as a magnitude which increases by unit steps, and can only, as now generally believed, be the atomic number, determined by nuclear charges of the element. But the absolute value of N has only been confirmed by the Bohr theory of the Hydrogen spectrum, according to which we know the absolute scale of measurement. Previous to the existence of this theory, Hicks and Rydberg showed independently that a better agreement with the experimental results, as they were then known, could be found by supposing the existence of elements with atomic weights between those of Hydrogen and Helium.

The difficulty thus defined continues to exist, however, in the case of the band-spectrum formula. No experimental information can be presumed to be sufficiently precise to allow a specification of the exact integer—in the quantum specification,—which really determines the wave-length of any component member, and only differences of such integers can be determined precisely. It follows that if a spectrum contains a term like $(m+\alpha)^2$, where m goes up in unit stages, the meaning and value of α are, at present, entirely undefined in any band spectrum. They change according to the value of m adopted, and, in this respect, Heurlinger's investigation

* Dissertation, Lund, 1918.

is strictly parallel to those of Rydberg and Hicks to which we have referred. And, at this point, the formula for band spectra, as a function of integers, becomes analogous to that for line spectra as originally given by Rydberg, who contended that the line spectra did not depend on integers, but on expressions of the form $(m + \mu)$, where m is an integer and μ an atomic constant whose nature could not be elucidated without an atomic model—with the consequence that the absolute value of m was also indeterminate.

We propose to suggest, leaving analytical treatment of the theoretical basis for a further paper, that the general formula for band spectra is of the type,

$$n = N' \left\{ \frac{1}{q + \mu + \alpha(m + \alpha_1)^2 + \beta(r + \beta_1)^2 + \dots} \right\}^2 - N' \left\{ \frac{1}{q' + \mu + \alpha(m' + \alpha_1)^2 + \beta(r' + \beta_1)^2 + \dots} \right\}^2,$$

where N' is a Rydberg constant, modified or not by a purely numerical multiplier; and (q, q', m, m', r, r') are integers. It is also presumed that $(\alpha_1, \beta_1, \dots)$ are at least approximately constants as regards the varying integers, and that the coefficients (α, β, \dots) are very small and dependent on the ratio m/M of the mass of an electron to that of a typical nucleus in the molecule.

The integers (q, q') arise as in the ordinary quantum theory applied to electronic orbits, but (m, m', r, r') are integers arising from the quantization of degrees of freedom of the nuclei. This, of necessity, confines the actual motions of the nuclei to a range dependent on m/M in comparison with the range of electronic motions, and the effect is therefore a multiplication of such a factor into any terms of the formula which involve these integers.

It is, of course, only contended that this is the appropriate first approximation to the true formula in exactly the same sense and with the same physical significance as Rydberg's form is the first approximation to line spectra.

From the smallness of α and β , a binomial expansion of the formula is possible in powers of (α, β, \dots) , and it follows that if (q, q') are kept constant, a Deslandres formula ensues approximately for passages between states characterized by variations only of the quanta inherent in nuclear motion. Moreover, a band head corresponds to specific constant values of the nuclear integers, and all the heads, as (q, q') vary, form a Rydberg line series. The formula, in fact, appears to conform to all the present existing knowledge of series relations.

In view of the preceding argument regarding the smallness of (α, β, \dots) it is very significant that bands due to the lighter elements are represented with much greater difficulty by a Deslandres formula, and, in fact, in the Fulcher bands of Hydrogen—the element for which m/M is greatest—no such formula can be regarded as quite satisfactory. The meaning would appear to be that α^2, β^2, \dots are no longer sufficiently negligible in the binomial development. Numerical investigation, which we do not consider it necessary to include in this paper, fully confirms this, and by retaining α^2 in the case of the Fulcher bands and in other spectra incompletely interpreted by Deslandres's simpler formula, we can find some of the constants if they are expressed in the new form suggested. The resulting values of α and q , in that form, are in all cases of the order of magnitude which would be expected for spectra given by such a formula in the visible region. This is a valuable confirmation of the type.

In conclusion, we may briefly indicate certain of the less general properties of some band spectra which theory must ultimately account for.

In the main, band spectra form three classes. Those of the first class fall off, or are degraded on one side only, red or violet, and come to a sharp end on the other side, with their head-differences arranged nearly in arithmetic progression, and the components associated with any head also so arranged. This group contains the majority of known spectra. In the second class, the heads degrade again on one side only, but the heads are not readily seen unless the dispersion is weak, and in other cases are in no respect outstanding and are perhaps not even visible. Some of the components of each band have, in this case, differences in arithmetical progression, but sometimes the differences are actually constant; other portions, again, may have no apparent order, although the individual bands of these components are precisely like the others. Secondary Hydrogen, in its lines which show no Zeeman effect, belongs to this class, and is probably the most difficult member to elucidate. Other cases are the band spectrum of Iodine, investigated by Hasselberg, and Croze and Birge's "first group of Nitrogen bands."

The third class of bands contains those which have no "heads" in the ordinary sense, but which degrade on both sides of the maximum intensity. These are found to follow a Deslandres formula on each side, reckoned from the maximum point as an origin.

Bands are known with a constitution yet more simple, but these are, ordinarily, absorption-bands of very complex compounds. Perhaps the most noteworthy are the very extensive absorption spectra of sulphurous acid and of toluene. In the former case, Baly and Garrett* have succeeded in representing the band by the formula

$$n = 33751.6 + 2.73m + 223.225\tau,$$

not involving the squares of the integers m and τ —but not thereby conflicting with the general suggestion of a formula we have made,—involving, in fact, very small α and very large α_1 , but no more extensive modification. This is a case of equidistant components, and the band degrades on both sides. In actual fact, sulphurous acid also has a group of bands in the ultra-violet, and six more, found by Coblentz, in the infra-red. All may be included in the single formula with three integers (s, m, τ),

$$n = 2.73m + 223.25\tau + 192.866s,$$

where m ranges from -44 to $+37$, n from -7 to $+13$, and

$$s = 5, 6, 7, 9, 13, 16, 175$$

—a very remarkable collection of integers. This formula can simultaneously represent 12,000 components. Baly and Garrett, in other papers, have applied certain quantum considerations to this band, but not, as we consider, in a form which is in accord with the general function of quanta in relation to spectra. At the same time, it is not to be presumed that such complicated and, if the term may be used, loosely-bound molecules as those of sulphurous acid necessarily behave in an analogous way to the simpler molecules with only two or three nuclei. It is noteworthy that all cases in which this simple type of law appears to be satisfactory appear to correspond to very complex molecules, as again in the case of toluene, and frequently to very unstable compounds like sulphurous acid, probably associated with water in a very large molecular aggregate. Such molecules provide, indeed, an extreme limiting case in one direction, and their study is not quite germane to our present object.

* *Phil. Mag.* xxxi. p. 512.

LXX. *Notices respecting New Books.*

Tables Annuelles de Constantes et Données Numériques de Chimie, de Physique et de Technologie. Vol. v., part 1 [pp. xli. + 804]. (English agents: Cambridge University Press; 1925. Price not stated).

THE fifth volume of the well-known tables of constants published under the patronage of the International Research Council and of the International Union of Pure and Applied Chemistry covers the literature of the years 1917 to 1922 inclusive. The next volume to appear will deal with the years 1923 and 1924. The liquidation of the arrears of publication arising during the War period will then have been completed, and thereafter annual publication will be resumed.

The first part of the fifth volume, published recently, contains over 800 pages; the data given have been extracted from more than 400 scientific journals and publications, and many additional publications, not enumerated in the volume, have been searched for relevant data. These figures emphasize not only the enormous volume of scientific work published in these days, but also the impossibility of collecting complete observational data relative to any particular point without tables of reference such as those under review. No scientific library can afford to be without these volumes.

Full references to the original publications are given throughout. The Table of Contents, printed in French, German, English, and Italian, is sufficiently detailed to enable the particular section in which the data required are given to be easily found. Cross-references are given where necessary. Readers of this Magazine desirous of obtaining more detailed information about the Tables, with specimen pages, can obtain such on application to the General Secretary, Dr. C. Marie, 9 Rue de Bagneux, Paris (VI.).

LXXI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xlix. p. 1080.]

January 21st, 1925.—Dr. J. W. Evans, C.B.E., F.R.S.,
President, in the Chair.

Dr. LÉON W. COLLET, For. Corr. G.S., Professor of Geology and Dean of the Faculty of Science in the University of Geneva, delivered a lecture on 'The Latest Ideas on the Formation of the Alpine Range.'

In 1905 Prof. E. Argand determined in the Pennine Alps the existence of six great recumbent folds or nappes. He started from the notion of the geosyncline, so splendidly developed by Dr. E. Haug, and destined to remain for all time the basal conception of tectonics. His equipment included a very detailed stratigraphical knowledge, and, armed with this, he has succeeded in straightening out the recumbent folds, and in thus reconstituting

the Pennine region at various stages of its development, when the general geosynclinal depression was subdivided by geanticlinal ridges.

On the base of Argand's results Dr. R. Staub found in the north-eastern part of the Swiss Alps the same tectonic elements, covered by six higher nappes belonging more to the type of the 'thrust-masses' of the North-Western Highlands of Scotland than to the type of the recumbent folds of the Pennine Alps. This new series of nappes has been named by Staub the Austrides, for they form the main part of the Austrian Alps.

For many years the Austrian geologists regarded the Tauern as a gneissic massif surrounded by schists and shales. Lately Prof. L. Kober, of the University of Vienna, has recognized instead a window: that is, a horizontal cut, due to erosion, in the nappes of the Austrides, which reveals deeper nappes belonging to the Pennine series. Therefore, this discovery shows that the nappes of the Austrides have been thrust over the Pennine nappes in the Austrian Alps, just as in the north-eastern part of Switzerland.

This was excellent, but a satisfactory co-ordination of the work done by Austrian and Swiss geologists was needed. That was accomplished at the end of last year by Dr. Staub. He published a memoir on the formation of the whole Alpine chain, from the French Alps to the Austrian, including the Swiss Alps, and summarized his views in a splendid geological map.

A capital point is the employment of Wegener's ideas on the drifting of continental masses, to explain the movement of the Hinterland towards the Foreland of the geosyncline. Foreland and Hinterland constitute the boundaries of the great Alpine geosyncline: together they recall the two jaws of a vice. Prof. P. Termier, Director of the French Geological Survey, has shown how the approach of the two jaws has led to the compression of the geosyncline, and thus to the development of the Alpine chain. Prof. Argand, at the Session of the International Geological Congress in Brussels, showed that the nappes of the Austrides belong to the Hinterland: that is, to Africa or Gondwanaland. Therefore the Austrides, with the Préalpes, represent a small part of Africa resting on Europe or Eurasia. These important views are accepted by Dr. Staub and by the Lecturer. Alpine tectonics are a great support to Wegener's theory on the drifting of continental masses.

The Lecturer presented the results arrived at, with the help of an enlargement of Dr. Staub's geological map, drawn by his Assistants for this lecture and others that he had arranged to give at the University of Cambridge, at the University College of Wales, Aberystwyth, and to the Geological Society of Edinburgh.

At the end of the lecture Prof. Collet showed lantern-slides with views of the Pennine Alps (to illustrate Argand's standard work) and views of the Mont Blanc Massif, where he has been working in recent years with his collaborators, Prof. Reinhard and Dr. Parejas.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]